ELEVATED TEMPERATURE MECHANICAL PROPERTIES OF LINE PIPE STEELS

by

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The effects of deformation temperature near the dynamic strain aging (DSA) regime on the tensile properties of X70 and X52 line pipe steels were evaluated. Testing temperatures of interest were in the range of 25 to 350 °C, at engineering strain rates in the range of approximately $10^{-4}$ to $10^{-3}$ s$^{-1}$. The X70 steel had a quasi-polygonal ferrite microstructure with austenite, martensite-austenite, and carbide microconstituents present. The X52 steel was a control material (anticipated to exhibit elevated temperature behaviors comparable to observations in the DSA literature) with a ferrite-pearlite microstructure.

Elevated temperature tensile testing was used to strain material and measure the mechanical properties of the X52 and X70 steels. Further mechanical and microstructural characterization was performed on the as-received and deformed line pipe steels, or in situ during elevated temperature deformation. Digital image correlation (DIC) was used in situ to characterize localized deformation behaviors during testing of the line pipe steels. Strain rate jump tests (cycling of strain rates during deformation) were performed to measure the temperature dependence on the instantaneous strain rate sensitivities. Stress relaxation tests were used to measure the internal/effective stress components of the flow stress and apparent activation volumes. Torsional pendulum experiments were performed to measure internal friction carbon Snoek peak heights related to the free interstitial concentrations in bcc ferrite. Microstructural changes after tensile deformation were assessed at various length scales using scanning and transmission electron microscopy. Finally, high sensitivity phase analyses were performed using synchrotron wide-angle x-ray scattering.

Both pipeline steels exhibited evidence of DSA under similar testing conditions. The DSA temperature regime for the X70 steel was slightly smaller than the DSA regime for the X52 steel. Manifestations of DSA during tensile testing (i.e. mechanical behavior within the DSA regime) include: serrated flow curves, stable localized deformation (in the form of propagating and nucleating deformation bands), increasing flow strength as a function of temperature, reduced ductility relative to room temperature, high strain hardening rates, high dislocation densities relative to room temperature, and negative strain rate sensitivities. There was a direct relationship between the flow curve morphologies and localized deformation band behaviors. Deformation band propagation was associated with relatively low frequency load drops in the flow curve and was typically observed at relatively low temperatures within the DSA regime. Deformation band nucleation was associated with relatively high serration frequencies and was typically observed at relatively high temperatures within the DSA regime. The critical strain required for serrated flow was greatest at the upper and lower boundaries for serrated flow. Negative strain rate sensitivities associated with samples tested within the DSA regime influenced necking.
behaviors in the pipeline steel tensile samples. Necking in samples that exhibited negative jump test strain rate sensitivity m-values was more concentrated (i.e. influenced a smaller portion of the gauge length) compared to samples with positive strain rate sensitivities. Necking initiated from previously propagating type deformation bands within the dynamic strain aging regime, and concentrated at a slightly higher rate than samples that exhibited uniform plastic deformation.

At high temperatures outside the DSA regime, the X70 steel exhibited tensile behavior that deviated from the X52 that was a result of strain assisted tempering of the quasi-polygonal ferrite microstructure (referred to as strain assisted bainitic tempering, due to the similarities in phase changes present between the two microstructures during tempering). Evidence of tempering of the quasi-polygonal ferrite microstructure was the decomposition of austenite observed with wide-angle x-ray scattering and scanning electron microscopy and the dissolution of transition carbides. Precipitation of cementite, which is associated with low temperature tempering, was theorized to contribute to the relatively high temperature mechanical behavior. Strain assisted bainitic tempering caused a shift in the flow stress maximum to higher temperatures (i.e. precipitation strengthening caused an increase in the flow stress), reduced ductility, increased strain hardening rates, negative overall strain rate sensitivities, increased interstitial carbon concentrations in the ferrite, increased apparent activation volumes, and increased dislocation densities. Austenite decomposition (which was used as the primary indicator of tempering in the quasi-polygonal ferrite microstructure) was highly strain dependent at temperatures below approximately 300 °C. However, increased temperatures reduced the strain dependence on austenite decomposition (and tempering), therefore reducing the strain dependence on carbide precipitation and coarsening (i.e. tempering occurred during isothermal heating, prior to deformation).

A theoretical X70 alloy (based on the steel used in the present study) was designed for optimized elevated temperature mechanical properties. It was theorized that maximum strengthening from strain assisted bainitic tempering could be achieved by retarding the coarsening of cementite precipitates in the quasi-polygonal ferrite grains. Additional carbide forming elements were added to the designed X70 alloy to retard cementite growth during tempering.
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Steam assisted gravity drainage (SAGD) is an extraction method for the recovery of bitumen (heavy oil), which is found in naturally occurring mixtures of sand or clay and water and has essentially no mobility in its natural state due to high viscosities (typically around $10^6$ cP) [1, 2]. A factor which promotes the use of thermal recovery processes, such as SAGD, is that many of the deposits of heavy crude oils are large, rich, and often well-known [3]. Figure 1.1 shows a schematic representation of the SAGD process. A well pair (two parallel pipelines placed in the same oil seam) is positioned in the bitumen deposit and secured with cement. Steam is injected into the bitumen at high pressure (3000-5000 kPa) at a rate of about $4 \times 10^5$ cm/h, reducing the viscosity by more than five orders of magnitude at temperatures above 200 °C [1–4]. Once the bitumen is at the extraction temperature (i.e. the temperature needed to extract the heavy oil), it is pumped to the surface through the producer well.

Due to significant economic advantages, there is increased demand for high pressure transportation of crude oil and gas over a range of operating temperatures. To accommodate demand, high strength-high toughness steels classified by The American Petroleum Institute (API) are used for large diameter line pipe. The use of high strength material such as API X70 (485 MPa minimum yield strength) facilitates design with significantly decreased wall thicknesses, allowing for economic benefits due to weight reduction during the transportation to remote locations, larger diameters for increased pressures, and manipulation of pipe during construction and welding [5, 6]. Line pipe steels typically contain low carbon contents to maintain good weldability [7, 8]. Due to low carbon concentrations, additional alloying elements are important to achieve the strength requirements of X70 steels, but alloying is limited to maintain cost efficiency [9].

It is important to understand the mechanical behavior of line pipe steels used for high temperature extraction operations to safely obtain the bitumen and ensure there is no contamination of aquifers or substantial ground movement between the surface and the oil rich zone. Operating temperatures of the SAGD process are typically in the range of 200-350 °C, while more conventional working conditions for line pipe steels include high pressures and low ambient temperatures [5]. There has been significant research concerning strength, ductility, and toughness of line pipe steels at low operating temperatures [5, 7, 10, 11], but limited work has been done to study elevated temperature properties of these steels.
1.1 Summary of Previous Findings

The current project was initiated as a master of science (MS) thesis [12] designed to characterize the elevated temperature mechanical properties of X70 line pipe steels in the range of 200-350 °C. The purpose of this section is to outline the key results of the MS thesis that provided the driving force for the PhD work, which was designed to build upon the previous MS research. A wider range of temperatures was tested since the publication of the MS work, and the results discussed below reflect the updated data set. Table 1.1 shows the tensile testing matrix of data generated for the MS and PhD work. The PhD project added 100, 150, and 400 °C testing conditions to the MS testing matrix to gain a better understanding of the temperature dependent properties.

![Figure 1.1](image_url) Schematic representation of the SAGD process. A well pair is used to inject steam into the oil seam and extract the bitumen to the surface (unpublished diagram from Evraz NA, provided in the project proposal). (Color image, the reader is referred to the .pdf version of this document).

Tensile and strain rate sensitivity testing were used to compare the mechanical properties of three commercially produced X70 steels, one of which is discussed in the present work because all three X70 steels exhibited similar behaviors compared to each other, and a control X52 steel. Data were obtained on the four steels to characterize material response to elevated temperatures near the DSA regime (more details on these materials and testing methods are provided in Chapter 3 and/or the MS thesis [12]).
initial hypothesis of the MS work was that the X70 steels exhibited evidence of dynamic strain aging (DSA) that was comparable to behavior that has been published in the steel literature.

Table 1.1 - Tensile Testing Matrix for X52 and X70 steels.

<table>
<thead>
<tr>
<th>( \dot{\varepsilon} ) (s(^{-1}))</th>
<th>25</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>225</th>
<th>250</th>
<th>275</th>
<th>300</th>
<th>325</th>
<th>350</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-4} )</td>
<td>M</td>
<td>P</td>
<td>P</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>P (X70)</td>
</tr>
<tr>
<td>( 8 \times 10^{-4} )</td>
<td>M</td>
<td>-</td>
<td>-</td>
<td>M</td>
<td>M</td>
<td>M</td>
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<td>M</td>
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</tr>
<tr>
<td>( 10^{-3} )</td>
<td>M</td>
<td>P</td>
<td>P</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>P (X70)</td>
</tr>
</tbody>
</table>

M = Testing condition from MS thesis.
P = Testing condition added for PhD study (only X70 tested at 400 °C).

From past literature, it is known that with an increase in temperature, contributions of DSA lead to serrated flow (observed in the stress-strain curve), a peak in the strain-dependent flow stress, a peak in the work hardening rate, a minimum in ductility, and a minimum in strain rate sensitivity (including the observation of negative strain rate sensitivities in the temperature region of serrated flow) [13–15]. In steels, the extent of DSA depends on interstitial carbon and nitrogen contents controlled by alloying and processing [13–25]. For more information on DSA the reader is referred to Chapter 2, and literature reviews from Richards [26] and the MS work [12] (which was written to compliment Richards document).

Figure 1.2 shows four example true stress-strain curves from the X70 material in the high strain rate condition tested at various temperatures around the DSA regime. More tensile curves from X70 and X52 steels can be found in the MS thesis [12]. Observations of serrated yielding in the flow curves (samples 205 and 249 °C) were the first indications of active DSA in these pipeline steels. The morphology of the flow curve during DSA reflects the behavior of stable, localized deformation bands that nucleate and propagate along the sample gauge length [15]. In the MS work, an attempt was made to characterize the morphology of the serrations based on a classification scheme developed by Rodriguez [15], but the observations were inconclusive. Robinson and Shaw [17] indicated that serrations in tensile curves that result from interstitial atom/dislocation interactions (as opposed to substitutional atom interactions) are irregular and not easily systematically analyzed. Also, characterization of deformation band behavior during DSA in steels has not been well documented in the literature [17].

Observations of either serrated yielding or continuous (uniform) plastic deformation were recorded for each temperature/strain rate condition in the pipeline steels and, engineering diagrams called serration maps were generated to characterize the DSA regime. A serration map is a plot of inverse absolute temperature and log strain rate used to predict if a temperature/strain rate deformation condition
will result in DSA [17]. The upper and lower bounds of the DSA regime are defined by linear lines on a serration map.

![Figure 1.2](image)

**Figure 1.2** Partial true stress-strain curves from the X70 steel (up to 0.07 true strain) showing 25, 205, 249, and 300 °C testing conditions at an engineering strain rate of $10^{-3}\text{ s}^{-1}$. Two different serration types are shown in the intermediate temperature conditions.

Figure 1.3 shows serration maps for the X52 and X70 steels. Note that 100, 150, and 400 °C testing conditions at $10^{-4}$ and $10^{-3}\text{ s}^{-1}$ strain rates have been added (i.e. conditions that were not discussed in the MS thesis, see Table 1.1) to the serration maps and figures presenting mechanical properties of the pipeline steels to gain a more complete understanding of the high temperature behaviors. Slight differences in the conditions which define the DSA boundaries for the two steels were observed. For example, the low strain rate 100 °C condition for the X52 steel exhibited serrations, while the X70 steel exhibited continuous plastic deformation. The differences between the X70 and X52 steels were slight and it was concluded that the conditions for DSA in the steels studied were approximately the same. Such a conclusion supported the initial hypothesis that the X70 steels had comparable mechanical behavior to studies reported in the steel DSA literature.

Figure 1.4 shows the temperature dependence of yield stress, flow stress at 0.05 true strain, and uniform elongation values for the X52 and X70 steels tested at $10^{-4}$ and $10^{-3}\text{ s}^{-1}$ engineering strain rates. The DSA regimes (defined by the serration maps in Figure 1.3) are indicated by the shaded regions for each data set. All materials studied in the MS thesis [12, 27] were reported to exhibit a decreasing trend in yield strength as a function of temperature. However, the more recently added 100 and 150 °C testing conditions for each strain rate revealed local maxima in yield strength within the DSA regime. Maxima in yield strength were associated with the manifestations of DSA in tensile data discussed by Leslie [13, 14] and Rodriguez [15].

Maxima in flow stress at 0.05 true strain were observed at all strain rates. For all samples, flow stress maxima were observed at greater temperatures than yield stress maxima. Flow stress maxima in the
X70 steels were also observed at greater temperatures than the maxima associated with the X52 steel at all strain rates. In X52 steels, flow stress maxima were observed at approximately the upper bound of the DSA regime. However, in X70 steels, flow stress maxima occurred at approximately 75 °C greater temperatures compared to the X52 control. Differences in testing conditions for flow stress maxima between the X52 and X70 steels were unexpected based on the approximately constant temperature/strain rate conditions for serrated plastic flow (see Figure 1.3).

![Figure 1.3 Serration maps for (a) X52 and (b) X70 steels. Open shapes indicate that continuous deformation was observed, and closed shapes indicate that serrated yielding was observed in the tensile flow curve. Lines indicate the upper and lower bounds of the DSA regime.](image)

Maximum flow stress values were compared to room temperature flow stress values to assess the greatest amount of strengthening in the temperature range of interest and the results are summarized in Table 1.2. At all strain rates tested, the X70 steels exhibited greater strengthening, as evident by calculated Δσ_{0.05} values at elevated temperatures, compared to the X52 steel.

<table>
<thead>
<tr>
<th>Material</th>
<th>Strain Rate (s(^{-1}))</th>
<th>σ_{0.05} (25 °C, MPa)</th>
<th>σ_{0.05} (Max, MPa)</th>
<th>T (σ_{0.05} Max, °C)</th>
<th>Δσ_{0.05} (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X52</td>
<td>10(^{-4})</td>
<td>482</td>
<td>513</td>
<td>250</td>
<td>31</td>
</tr>
<tr>
<td>X70</td>
<td>10(^{-4})</td>
<td>638</td>
<td>720</td>
<td>325</td>
<td>82</td>
</tr>
<tr>
<td>X52</td>
<td>10(^{-3})</td>
<td>488</td>
<td>503</td>
<td>275</td>
<td>15</td>
</tr>
<tr>
<td>X70</td>
<td>10(^{-3})</td>
<td>639</td>
<td>690</td>
<td>350</td>
<td>51</td>
</tr>
</tbody>
</table>
Both X52 and X70 steels exhibited decreased ductility (compared to room temperature) in the DSA regime at all strain rates tested. At high temperatures outside the DSA regime, steels in the literature [13–25, 28–41] and the X52 steel exhibited increasing ductility with increasing temperature. In contrast, ductility maxima were observed in the X70 steels around 275 °C at $10^{-4}$ s$^{-1}$ and 325 °C at $10^{-3}$ s$^{-1}$. The decrease in ductility around 300 °C (which produced the maxima observed) and increased temperature for maximum flow stress were considered to be unassociated with DSA, indicating that currently unidentified metallurgical phenomena could have contributed to the mechanical property trends observed in the X70 steels (possibilities considered in the MS thesis are discussed below). The greater increases in elevated temperature strength in the X70 compared to the X52 steels (Table 1.2) also indicated that strengthening.
mechanisms that contribute to the flow strength of pipeline steels require further characterization and analysis. The total amount of strengthening from DSA alone cannot be directly compared since the total interstitial concentrations of the X52 and X70 steels were not quantified.

Strain rate sensitivity measurements were also used to assess DSA in the pipeline steels. Strain rate sensitivity m-values were calculated using

\[ m = \frac{\log(\sigma_2/\sigma_1)}{\log(\dot{\varepsilon}_2/\dot{\varepsilon}_1)} \]  

where \( \sigma \) is the flow stress measured under a known strain rate and \( \dot{\varepsilon} \) is the strain rate imparted on the tensile bar. Stress pairs measured require constant temperature and strain for m-value measurements to be valid. Two methods of measuring strain rate sensitivities were used. The first method used flow stress values at 0.05 true strain, measured directly from the tensile data (plotted in Figure 1.4) and the second method was the strain rate jump test (detailed by Wagoner [42] and Dieter [43]). Detailed information on procedures, advantages, and disadvantages for both m-values measured have been outlined in the MS thesis [12]. The primary advantage of the jump test is that only one tensile specimen is needed to calculate an m-value, eliminating error that comes from statistical deviations between samples that arise from the flow stress measurement method. Flow stress m-values still provide useful information. Dislocation substructures in jump tests deviate from substructures generated in a standard tensile test, and m-values measured with the flow stress method can be measured at any strain. Figure 1.5 shows examples of how m-values were measured with each testing method. Several strain rate jumps were performed during testing. Up-jump (low to high strain rate transition) m-values at approximately 0.05 true strain were used for the bulk of the analysis. Peaks and valleys observed in the jump test data were a result of material acceleration from the tensile frame changing crosshead speeds. Each strain rate was held constant for enough time to allow for steady state deformation to continue and the tensile curve was extrapolated back to the strain location of the jump, where flow stresses were measured, and an m-value was calculated.

Figure 1.6 shows the temperature dependence of strain rate sensitivity m-values measured from both jump test and flow stress methods for X52 and X70 steels. Both materials exhibited approximately the same temperature dependent functionalities in the jump test results. Negative m-values were observed for all jump test curves that exhibited serrations at either strain rate around 0.05 true strain and positive m-values were observed for all other tests. Distinct transitions from negative to positive strain rate sensitivities were observed at temperatures between 250 and 275 °C (Just past the upper bound of the DSA regime measured in Figure 1.3). The transitions from negative to positive strain rate sensitivities were likely a direct result of DSA behavior based on comparisons with the literature [15, 28, 31, 32, 44, 45].
Figure 1.5  Examples of jump test (top) and flow stress (bottom) m-value measurements. The examples used are from the X70 steel tested at approximately 300 °C. Stress pairs at 0.05 true strain used for calculated m-values are schematically shown by the circles.

Flow stress m-values measured in the X52 steel exhibited a more gradual transition from negative to positive strain rate sensitivities. However, the behavior had close similarities compared to the jump test results. X52 m-values at 275 and 300 °C were near zero and considered to be the location of a transition from negative to positive strain rate sensitivities when the statistical deviations in properties between tensile specimens were accounted for. Flow stress m-values measured in the X70 steels exhibited different behaviors compared to the X52 steel or the jump test results. Strain rate sensitivities of the X70 steel exhibited a transition from negative to positive m-values at a greater temperature than both the jump test results for both materials and flow stress data for the X52 steel. It is currently unknown why the jump test and flow stress measurement methods produced such different results in the X70 steel. Due to negative strain rate sensitivities, it is hypothesized that phenomena that are yet to be identified likely have a time dependent response to influence strength (e.g. low strain rates allow more time for diffusion based processes which can result in negative m-values).
Figure 1.6 (a) Jump test and (b) flow stress m-values measured at 0.05 true strain for X52 and X70 steels. The shaded region defines the average DSA regime based on the observation of serrations in the flow curves.

Figure 1.7 shows another important observation from the MS work regarding the temperature dependence of deformation anisotropy. Results of these observations were determined by studying fracture surface geometries (Figure 1.7a) of circular cross-section tensile specimens and are included in the MS thesis [12] and an accompanying publication [46]. An anisotropy parameter of the ratio of minor diameter to major diameter of the oval shaped fracture surface was created to assess the degree of anisotropy (low anisotropy parameter values indicate high levels of anisotropic deformation). A minimum in the degree of anisotropic deformation (maxima in anisotropy parameter) was observed at approximately 300 °C. The observed minima in anisotropic deformation aligned with flow stress and elongation maxima in the X70 steels. It was hypothesized [46] that strengthening imparted by DSA (and phenomena at slightly greater temperatures) is orientation dependent and varies with the degree of crystallographic texture.

Tensile properties were also investigated after a 100 h low temperature aging (LTA) heat treatment under a tensile stress of 419 MPa (approximately 75 pct of the room temperature yield
strength). The LTA experiments were performed to simulate potential effects of exposure under stress at temperatures characteristic of line pipe steels in elevated temperature oil extraction processes. Samples were heat treated in a creep frame and aged at temperature of 200, 275, and 350 °C. After aging, the tensile samples were tested at the LTA temperatures at an engineering strain rate of $8.3 \times 10^{-4}$ s$^{-1}$.

Figure 1.8 shows partial engineering stress strain curves for both as-received and LTA tensile specimens for the X70 steel. At 200 °C, both specimens exhibited serrated plastic flow from DSA, and the two higher temperature conditions exhibited continuous plastic deformation. All LTA specimens exhibited increased yield strength compared to the as-received conditions. The increase in yield strength was attributed to static strain aging (evident by the observation of YPE in all LTA flow curves). However, only the 200 and 275 °C LTA conditions exhibited increased flow strength compared to as-received samples. At 350 °C, the LTA specimens exhibited lower strain hardening rates (qualitatively identified by the slope of the engineering stress strain curves at any given strain), which resulted in decreased flow stresses in the LTA samples at strains greater than approximately 0.01 engineering strain compared to the as-received condition.

![Figure 1.7](image1.png)

**Figure 1.7** (a) Engineering stress-strain curve and fractograph of an X70 specimen tested at 200 °C and an engineering strain rate of $8.3 \times 10^{-4}$ s$^{-1}$. Fractograph of the fractured tensile specimen shows the oval shaped fracture surface with $D_{\text{Major}}$ and $D_{\text{Minor}}$ measurements (used to measure the anisotropy parameter) schematically shown. (b) Temperature dependence of the anisotropy parameter ($D_{\text{Minor}}/D_{\text{Major}}$) for all strain rates and temperatures tested [46].

Figure 1.9 compares the 0.2 pct yield strength, ultimate tensile strength (UTS), uniform elongation, and total elongation measurements as a function of temperature for the LTA and as-received testing conditions of the X70 steel. LTA measurements are indicated with open shapes and as-received measurements are indicated with closed shapes. At all temperatures, the LTA conditions exhibited yield
strength measurements greater than the as-received yield strengths. The LTA conditions exhibited increased UTS at 200 °C, no observable difference in UTS at 275 °C, and decreased UTS at 350 °C compared to the as-received testing conditions. There was also no observable difference in ductility for both the LTA and as-received tensile specimens.

![Engineering Stress-Strain Curve](image1.png)

Figure 1.8 Partial engineering stress-strain curves (up to 7 pct strain) for as-received and LTA X70 tensile specimens [27].

1.1.1 Research Objectives

The main objective of the current work was to characterize the mechanical properties of X70 line pipe steels at temperatures industrially relevant to the SAGD process. The research objectives outlined in the current document reflect areas of interest based on results obtained during the MS project. Results from the MS work [12] indicated that X70 steels exhibited DSA, which influenced the strength, ductility, and deformation behavior at elevated temperatures. Strength, ductility, strain rate sensitivity, and anisotropic deformation behaviors were successfully characterized [12, 27, 46]. However, greater fundamental understanding of mechanical behavior was desired with respect to localized deformation during DSA and the unexpected X70 strength, ductility, strain rate sensitivity, and anisotropic deformation properties observed at temperatures around 300 °C.

The first objective of the PhD work was to correlate physical deformation behavior to the flow curve morphologies of steels in the DSA regime. As mentioned in the previous section, characterization of localized deformation behaviors at various conditions within the DSA regime were attempted in the MS work by analyzing serration morphologies and comparing them to a system described by Rodriguez [15] for materials that use substitutional atoms for DSA (e.g. 316 stainless steel or aluminum-magnesium alloys). The results were inconclusive, because the serration morphologies were challenging to analyze.
and compare to the literature. It was hypothesized that steels (which use interstitial atoms for DSA in the temperature range of interest) exhibit the same deformation band nucleation and propagation behaviors as materials with substitutional atoms contributing to DSA. The hypothesis was tested using digital image correlation (DIC) to study localized deformation \textit{in situ} during plastic deformation within the DSA regime.

![Figure 1.9](image_url)

\textbf{Figure 1.9} The influence of temperature on (a) yield and ultimate tensile strength and (b) elongation measurements in X70 for as-received and LTA tensile testing conditions [27].

The second objective of the PhD work was to identify metallurgical phenomena in the X70 steels that contribute to the mechanical behavior observed at high temperatures, just outside the DSA regime. Hypothesized possible phenomena included: DSA, precipitate coarsening, dynamic precipitation of carbides and/or nitrides, tempering of martensite in MA constituent, bainitic tempering of the quasi-polygonal ferrite microstructure, and strain induced transformation/decomposition of retained austenite. Although the presence of DSA was verified using tensile testing, the possibility of DSA that produced very low amplitude serrations (within the background noise of the load cell) outside the perceived DSA regime was considered. The X70 steels contained a significant amount of microalloying elements which can form carbides and nitrides. Bainitic microstructures can also have cementite (Fe₃C) and transition carbides within the microstructure. The presence of carbides/nitrides can contribute to increased strength via precipitation strengthening. Elevated temperatures and strain could provide enough energy for precipitate coarsening, which (depending on the size of the precipitates already present) could increase or
decrease the magnitude of precipitate strengthening. Okamoto et al. [40] proposed that dynamic precipitation could occur in high temperature testing conditions that exhibit smooth plastic flow and high strain hardening rates. The presence of retained austenite in the microstructure leads to the possibility of either strain induced transformation induced plasticity (TRIP) or the decomposition to phases closer to equilibrium conditions.

All the hypothesized phenomena discussed above were considered in the design of experiments for the second objective of the PhD work. Synchrotron wide angle x-ray scattering (WAXS), transmission electron microscopy (TEM), stress relaxation, and internal friction analysis techniques were selected to study changes in microstructure, internal/effective stress components, and interstitial defect concentrations in X70 and X52 steels before and after elevated temperature plastic deformation. Developing a greater fundamental understanding of why X70 steels exhibit more favorable mechanical properties at elevated temperatures compared to ferrite-pearlite steels will enable further improvement of steel alloying and processing for temperature applications up to 350 °C.

1.2 Overview of the Thesis

The literature review in Chapter 2 provides an overview of X70 line pipe steel alloying, processing conditions, and microstructure. Background information on DSA are provided regarding manifestations in tensile data, localized deformation behaviors, and the use of digital image correlation to study localized deformation. Dynamic strain aging studies where dynamic precipitation was potentially observed in bainitic and martensitic steels are outlined. Finally, background is provided on phase/dislocation density analysis with synchrotron x-ray diffraction, stress relaxation measurement methods for measuring thermal and athermal components of the flow stress, and internal friction techniques used to characterize interstitial/dislocation interactions.

The experimental design and procedures used to achieve the project objectives are detailed in Chapter 3. Materials selection and compositional information are included. Experimental methods regarding elevated temperature tensile testing are included first, as all testing techniques were designed around characterizing pipeline steels deformed at various temperatures. Detailed procedures on digital image correlation, stress relaxation, x-ray diffraction, transmission electron microscopy, and torsional pendulum internal friction are also included.

Chapter 4 includes results and discussion on understanding relationships between flow curve morphologies and physical deformation behavior during elevated temperature tensile deformation. Digital image correlation was used to characterize nucleation/propagation of deformation bands and plastic instability geometries. A classification scheme was developed to systematically relate localized deformation behavior to flow curve morphologies. The temperature and strain rate conditions for different
deformation behaviors was also discussed. Conclusions in Chapter 4 are directly related to the first PhD objective to relate flow curve morphologies to physical deformation behavior.

Chapters 5 through 8 include results and discussions on stress relaxation, x-ray diffraction, microscopy, and internal friction analyses independently. Conclusions were developed in the chapters that include independent characterization techniques. However, many of the techniques included in Chapters 4 through 8 complement each other. Discussions regarding all data generated in the MS and PhD work used to develop a better fundamental understanding of metallurgical phenomena that influence mechanical properties in pipeline steels at temperatures up to 350 °C (i.e. the second PhD objective) are detailed in Chapter 9.

Chapters 10 and 11 include overall conclusions and recommended future work regarding the mechanical properties of pipeline steels. The subsequent chapters include appendices with information that complements the results discussed in the body of this document.
CHAPTER 2

LITERATURE REVIEW

This chapter includes literature reviews on X70 steels, dynamic strain aging (DSA), digital image correlation (DIC) incremental strain analysis, dynamic precipitation (observed in DSA studies), synchrotron x-ray diffraction, stress relaxation testing, and internal friction testing. The reader should note that the literature review sections on X70 steels and DSA are summaries and updates to the sections included in the MS thesis [12]. The reader is also referred to Richards [26] thesis for more information on DSA, as the content in the MS thesis sections were designed to complement Richards work.

1.3 X70 Line Pipe Steels

Due to significant economic advantages, there is increased demand for the high-pressure transportation of crude oil and gas over a range of operating temperatures. To accommodate demand, high strength-high toughness steels classified by The American Petroleum Institute (API) are desired for large diameter line pipe. Use of high strength material such as API X70 (485 MPa specified minimum yield strength) steels facilitate pipeline design with significantly decreased wall thicknesses, allowing for economic benefits due to weight reduction during the transportation to remote locations, larger diameters for increased pressures, and manipulation of the pipe during construction and welding [5, 6].

Line pipe steels typically contain low carbon contents to maintain good weldability [7, 8]. Due to low carbon concentrations, additional alloying elements are important to achieve the minimum strength requirements for X70 specifications, but alloying is limited to low concentrations to maintain production cost efficiency. Manganese is a common alloying element in steels because it is an austenite stabilizer and it increases strength through solid solution strengthening. Microalloying elements (vanadium, niobium, and titanium) are added in small concentrations (typically less than 0.2 wt pct) to increase strengthening through grain size refinement achieved during thermomechanical processing, solid solution strengthening, and precipitation strengthening [9].

Initial line pipe steels consisted of ferrite and pearlite (a lamellar two-phase ferrite and cementite microconstituent) microstructures based on carbon and manganese additions [47]. However, steels with ferrite-pearlite microstructures cannot meet minimum strength and toughness specifications for X70. The addition of thermomechanical processing (TMP), accelerated cooling, and microalloying to line pipe steels has significantly increased strength [6–8, 47–49]. Processing parameters for TMP, such as soaking temperature, rolling temperature, deformation schedule, finishing temperature, and cooling rate play an important role in the final microstructure of the line pipe. Typical TMP microstructures consist of multiple microconstituents including ferrite, pearlite, acicular ferrite, polygonal ferrite, quasi-polygonal
ferrite, granular bainite, bainitic ferrite, martensite-austenite (MA) islands, retained austenite (RA) islands, and degenerated pearlite [7, 8, 50–52].

Figures 2.1 and 2.2 show example micrographs of some possible bainitic microstructures. Quasi-polygonal ferrite (Figure 2.1a) is observed in low to ultra-low carbon steels and forms by rapid cooling from single phase-austenite to single phase ferrite without a composition change. Cooling must be fast enough to minimize partitioning of alloying elements in the two-phase austenite-ferrite field. Quasi-polygonal ferrite grains typically show etching substructure and grain boundaries are typically irregular when compared to polygonal ferrite microstructures [52]. A finer grained quasi-polygonal ferrite microstructure with MA and RA constituent is shown in Figure 2.2. The MA and RA constituents were identified with a specialty color etchant used to identify martensite and austenite in steels.

![Micrographs](image)

Figure 2.1 Light optical micrographs of (a) quasi-polygonal ferrite formed in an ultralow-carbon steel containing 0.005 C and 3 Mn (wt pct) cooled at 50 °C/s, (b) acicular ferrite formed in HSLA-80 steel by isothermal transformation at 500 °C for 5000 s, and (c) granular ferrite formed in a modified A-710 steel continuously cooled at a rate of 1 °C/s [52].

Acicular ferrite (Figure 2.1b) is also observed in low to ultra-low carbon steels at high cooling rates, but the transformation temperature is lower than that of quasi-polygonal ferrite. Acicular ferrite microstructures consist of non-equiaxed ferrite grains with low angle grain boundaries (misorientation angles between 5° and 10°) [53]. Equiaxed morphology MA and RA islands are also common in acicular ferrite microstructures.

Granular ferrite or granular bainitic ferrite (Figure 2.1c) have many similarities to acicular ferrite and quasi-polygonal ferrite, but there are differences in microstructural morphologies. Granular ferrite
forms in the intermediate austenite transformation range and has a high dislocation density, but the cooling rate to form granular ferrite is slower than that of acicular ferrite [52].

![Image](image.png)

**Figure 2.2** Light optical micrograph, etched with LaPera’s color etchant, of an API X70 steel with an acicular ferrite (described as quasi-polygonal ferrite in the present work) microstructure containing MA (black) and RA (white) constituents [54]. *(It should be noted that the steel in this micrograph is the same X70 plate used in the present research).* (Color image, the reader is referred to the .pdf version of this document).

Fine grained TMP microstructures with dispersed MA islands are considered to have optimum strength, toughness, and weldability, as well as low ductile to brittle transition temperatures [7, 8, 47, 49, 53]. The properties of these microstructures are mainly due to relatively fine grains and high dislocation densities [53]. However, line pipe steels with bainitic microstructures have anisotropic mechanical properties (differences in strength, ductility, and toughness in different orientations of the plate) that can be related to crystallographic texture [53–57]. Crystallographic texture is defined as a condition in which the distribution of crystal orientations is nonrandom [58], and is caused by deformation, recrystallization, and phase transformations during steel processing [57].

1.4 **Dynamic Strain Aging**

The SAGD process operates at temperatures between 200 and 350 °C. In this temperature range, a solid solution strengthening mechanism, known as dynamic strain aging (DSA), is commonly observed in most steels. Leslie [13, 14, 16] defines DSA as the changes in properties of a metal that occur when point defects (interstitial atoms in bcc steels) and dislocations interact during plastic deformation. Static strain aging is similar to DSA and occurs when point defects interact with dislocations before plastic deformation. Carbon and nitrogen contribute most significantly to strain aging in steels, however, boron, hydrogen, and oxygen interstitial atoms have also been considered in the literature [20, 21].

17
In 1949, Cottrell and Bilby [59] developed a model that describes the strain aging phenomena that is considered correct and outlined in further detail by Reed-Hill [60] and Leslie [13, 14]. The Cottrell and Bilby model [59] deals with time and temperature dependence on formation of solute atmospheres near dislocations. For the solute atoms to interact with dislocations during deformation, there must be enough thermal energy and time for the solute atoms to diffuse to dislocation cores. For DSA to occur, solute atoms must be mobile enough to make at least one diffusive jump while deformation takes place.

When the temperature of the specimen is in the range where DSA is active, dislocations generated during deformation are quickly pinned so that others must be generated in order for deformation to continue [13]. Figure 2.3 is a plot of dislocation density as a function of strain for a steel strained at room temperature and at 200 °C (within the DSA regime). For all instances of strain, the material tested in the DSA regime had a higher dislocation density than the material tested at room temperature.

![Dislocation density versus plastic strain](image)

Figure 2.3 Dislocation density versus plastic strain for a 0.03 wt pct carbon rimmed steel tested in tension at a strain rate of 3.3 x 10^{-4} s^{-1} at room temperature and 200 °C [13].

Leslie [13, 14] and Rodriguez [15] have developed a list of manifestations of DSA behavior during tensile deformation. Figure 2.4 shows a schematic representation for all the manifestations described by Rodriguez.

1. The stress strain curve exhibits serrated yielding (load drops or discontinuities in the flow curve).
2. A peak in the variation of flow stress (σ) with temperature.
3. A peak in the variation of work hardening (\( \theta = \Delta \sigma / \Delta \varepsilon \)) with temperature (i.e. DSA results in relatively high work hardening rates compared to non-DSA conditions). 
4. A peak in the variation of the Hall-Petch slope (K_ε) with temperature.
5. A minimum in the variation of the ductility with temperature.
6. A minimum in the strain rate sensitivity (m or γ), with negative strain rate sensitivities in the temperature region of serrated flow.

Figure 2.4 Schematic illustration of the various temperature dependent manifestations of DSA as described by Rodriguez [15]. Progression of serration types are outlined at the bottom of the schematic. Strain rate sensitivities as a function of stress and/or strain are also schematically illustrated for various temperature conditions.

A more detailed analysis of the DSA literature [13–25, 28–41] indicates that maxima in flow stress generally occur near the upper bound of the temperature range in the DSA regime, there is a positive correlation between elongation and temperature outside the DSA regime, and there is a distinct
The transition from negative to positive strain rate sensitivities that accompanies the transition from serrated to uniform plastic flow.

The presence of DSA is dependent on having the correct combination of both temperature and strain rate, which influences diffusivity of point defects interacting with the mobile dislocations [17]. Low temperatures (and high strain rates) do not allow interstitial solute atoms enough time to diffuse to dislocation cores during deformation. At high temperatures (and low strain rates), solute atoms are very mobile relative to dislocation velocities and the DSA effect is not observed. The temperature-strain rate regime for DSA is typically defined by serration maps, which are engineering diagrams of log strain rate and inverse absolute temperature that indicate continuous or serrated plastic flow under various testing conditions. Figure 2.5 shows an example of a serration map for a low carbon steel [15]. Lines on the serration map indicate the upper and lower bounds of the DSA regime (region 1). The slopes of the boundary lines of the serration map are related to the activation energy (Q) for dynamic strain aging by the Arrhenius equation

\[
\ln(\dot{\varepsilon}) = \ln(\text{constant}) - \frac{Q}{R} \left(\frac{1}{T}\right)
\]  

where \(\dot{\varepsilon}\) is the strain rate, \(Q\) is the activation energy for dynamic strain aging, \(R\) is the universal gas constant, and \(T\) is the absolute temperature [38].

Figure 2.5 Serration map of a 0.03 wt pct carbon steel. 1 indicates the observation of serrated yielding (or DSA) in the tensile curve and 0 indicates the observation of uniform deformation [15].
1.4.1 Serrated Yielding and Localized Deformation

While DSA is active, stable localized plastic deformation (i.e. localized deformation without necking) occurs in the gauge length of the tensile specimen. Deformation markings are often visible on polished tensile samples and are commonly referred to as deformation bands, stretcher-strain markings, Portevin-Le-Châtelier (PLC) bands, or Luders bands [17]. Deformation bands can either propagate or nucleate within the tensile specimen. Propagation and nucleation behavior of deformation bands are directly related to the morphology of the serrations in the tensile curve. Rodriguez [15] and Robinson and Shaw [17] discussed the most common naming system used in the DSA literature [15, 17, 18, 34, 38, 61–72] for serrated yielding. The naming system was used to identify different types of serrations based on flow curve morphology and the behaviors of observed deformation bands were outlined [15]. The serrated yielding morphologies and deformation band behaviors have been well documented in the DSA literature [15, 17, 38, 70, 71] for materials that exhibit interactions between substituational atoms and dislocations during DSA. However, serrations caused by interstitial atom-dislocation interactions (e.g. bcc steel systems) were reported to be irregular and not easily systematically analyzed [17].

Figure 2.6 is a schematic representation of the Rodriguez system for identifying types of serration morphologies (labeled as Types A-E) associated with DSA [15, 17]. The type of serrated yielding observed is dependent on the material system and the temperature-strain rate conditions of a tensile test. It is possible for a material to exhibit all five types of serration morphologies under different temperature/strain rate conditions. Note, the serrations depicted in Figure 2.6 are based on observations from DSA caused by substituational atom-dislocation interactions.

Localized deformation from DSA has been studied using various methods in the DSA literature. Deformation bands have been studied using highly polished tensile specimens [17, 38], strain gauges located along the gauge length [38, 66], and more recently, thermal imaging [69, 73, 74] and DIC [65, 66, 68–72]. Deformation bands observed in polished samples are often difficult to detect, especially at elevated temperatures with samples that develop oxide layers on the surface during testing. Strain gauge methods do not have as high of resolution for analyzing localized deformation compared to thermal imaging or DIC.

Deformation bands can either propagate or nucleate in the tensile sample. Figure 2.7 shows a schematic representation of the relation between deformation band behaviors and serration morphologies (refer to Figure 2.6) outlined by Rodriguez [15]. The boxes on the tensile samples represent deformation band locations at a given strain (point along a stress-strain curve). Diagonal arrows represent the propagation of deformation bands and vertical arrows indicate nucleation events.
Figure 2.6  Schematic stress-strain curves demonstrating the different types of serrated yielding morphologies associated with DSA and the relative critical strain associated with each type. Figure was first published by Rodriguez [15] and was later re-drawn by Robinson and Shaw [17].

Type A deformation bands initially tend to nucleate at the one end of the specimen and propagate along the entire gauge length, then re-initiate at the original starting point. Type B deformation bands are an example of nucleation without propagation and occur in quick succession due to discontinuous band propagation (i.e. new bands appearing at the front of previous ones). Descriptions of Type B behavior were difficult to interpret. However, Type B deformation bands often accompany Type A or Type D bands, and are interpreted to consist of nucleation events that are constrained to occur at locations near previously deformed areas (giving the overall appearance of propagation behaviors, refer to Figure 2.7 for an example of Type A + B). Renard et al. [68] observed deformation bands from Type C serrations to nucleate chaotically, discontinuously, and in a non-correlated way. Type D deformation bands are thought to be similar to Type A [15], indicating that their deformation band behavior is likely unidirectional propagation along the gauge length. Type E deformation bands, studied by Anjabin et al. [70], were observed to continuously propagate back and forth along the gauge length (note Anjain et al. referred to these serrations as Type D, but the flow curve shape closely matches Rodriguez’s Type E).
Figure 2.7 Schematic representation of correlations between band behaviors and serration morphologies described by Rodriguez [15]. Red boxes represent deformation bands, diagonal arrows indicate band propagation, vertical arrows indicate band nucleation events. (Color image, the reader is referred to the .pdf version of this document)
1.4.2 Digital Image Correlation: Using Incremental Strain Analysis to Study Localized Deformation

Digital image correlation uses a series of photographs taken during deformation of a test specimen coated with a speckle pattern of randomly sized and spaced dots. During plastic deformation of the sample, the dots in the speckle pattern displace and deform (with the material) and surface strain is calculated locally by measuring relative planar-displacements between dots in two images associated with different strain values. Two types of strain measurements are possible with DIC. The first (engineering strain) is used when total accumulated strain is of interest and the second (incremental strain) is used when studying localized deformation. Engineering strain is measured by comparing an image of the strained sample to an image of the unstrained sample. Incremental strain is measured by comparing two images of the strained sample at different strains in a known time interval.

Localized deformation has been studied with DIC in metals that exhibit yield point elongation (YPE), DSA, and twinning induced plasticity (TWIP) during tensile testing using incremental strain analysis [65, 66, 68–70, 72–74]. Figure 2.8 shows an example of an incremental strain analysis from Anjabin et al. [70]. The material tested by Anjabin et al. [70] was a supersaturated AA6061 age hardenable aluminum alloy that exhibited DSA at room temperature. Serrated yielding was observed in the tensile data (Figure 2.8a) and localized deformation was observed in the incremental strain maps (Figure 2.8b) indicated by a color change from green to purple where the strain occurred in each time increment of 0.4 s. The force-time curve in Figure 2.8a shows evidence of Type A serrations transitioning to Type E serrations at higher strains (refer to Figure 2.6 for comparison of serration morphologies). Note, Anjabin et al. referred to the high strain serrations as Type D, however, the morphology more closely resembles Rodriguez’s Type E. The localized deformation behaviors of both (A and E) serration types closely matched the behaviors described by Rodriguez [15] that were depicted in Figure 2.7. Type A deformation band behavior, studied by Benallal et al. [66] with DIC, was also identical to the behavior observed by Anjabin et al. [70] and Rodriguez [15].

Renard et al. [68] studied localized deformation in an austenitic TWIP steel using different time increments based on load drop frequencies (of serrations) in the flow curve. Incremental strain maps were used to observe the movement of deformation bands during tensile testing. The deformation bands were also analyzed by plotting the strain distribution along a section of the DIC map parallel to the tensile axis, resulting in a peak where the localized deformation was observed. Figure 2.9 shows a partial true-stress-strain curve (exhibiting Type B serrations) with incremental strain maps associated with strain increments indicated by the arrows and the corresponding strain profiles along the tensile axis. Localized deformation bands were observed in the DIC incremental strain maps. The strain profiles (Figure 2.9b) resulted in a
peak in incremental strain that was associated with the localized deformation and approximately zero incremental strain along the rest of the gauge length.

Figure 2.8  
(a) Force-time curve showing Type A and E serrations (note, Anjabin referred to the high strain serrations as Type D, however they have a closer morphology to Rodriguez Type E) and (b) DIC incremental strain maps of a supersaturated AA6061 age hardenable aluminum alloy (0.846Mg, 0.631Si, 0.199Cu, 0.368Fe, and 0.2Cr, in wt pct) tested at room temperature and a strain rate of $10^{-3}$ s$^{-1}$. Adapted from Anjabin et al. [70]. (Color image, the reader is referred to the .pdf version of this document).
The time increment and strain rate are particularly important parameters for incremental strain analysis with DIC. Three serrations were analyzed in Figure 2.9 and two different strain increments were compared. The larger strain increment was set to span three serrations and the smaller strain increments covered single load drops. Three deformation bands were observed in Figure 2.9 using the small strain increment analysis (one for each load drop). However, the three peaks in the incremental strain profiles appeared very close together on the tensile specimen and the larger strain increment profile gave the appearance of a single deformation band (i.e. one peak of relatively greater height and width). It is therefore important to consider serration frequency when performing incremental strain analysis, as large strain increments (relative to serration frequency) can mask the appearance and behavior of the localized deformation bands. Ideally, the time increment used for DIC analysis is two times the frequency of the serrations observed in the tensile test so individual deformation bands can be detected. Resolving individual deformation bands can be limited to the image resolution and frame rate capacities of the DIC equipment and testing setup.

1.4.3 Dynamic Precipitation Observed in Dynamic Strain Aging Studies

It was hypothesized in Chapter 1, that dynamic precipitation occurred at testing temperatures greater than 300 °C (just outside the DSA regime) in the X70 steels and resulted in increased strength and decreased ductility. Dynamic precipitation is referred to as the precipitation of carbides or nitrides during
plastic deformation. Richards [26] and Okamoto et al. [40] have published studies of DSA in steels and observed functionality differences in flow strength and ductility with temperature when compared to the majority of the DSA literature in steel [15, 17, 18, 34, 38, 61–72]. It should be noted that dynamic precipitation was hypothesized by Okamoto et al. [40] and Richards [26] to explain mechanical property observations. However, little work has been done to verify the phenomena and characterize the precipitates and there is little published research on dynamic precipitation observed at temperatures and strain rates where DSA is an active strengthening mechanism.

Richards [26] observed potential dynamic precipitation when measuring flow strength as a function of temperature for a non-traditional bainitic steel (which consisted of elongated ferrite grains with martensite-austenite islands present), and selected results for temperature dependent flow stress at strains between 0.2 pct and uniform strain (ultimate tensile strength) are shown in Figure 2.10. The flow strength data at 3 pct and 5 pct strain exhibited two maxima. One maxima, located at 200 °C was attributed to DSA. The other maxima, around 300 °C, was potentially a result of dynamic precipitation. The high temperature peak was only observed at higher strains, which suggests that the phenomena that contributed to the increased strength (possibly dynamic precipitation) requires both elevated temperatures and strain to occur.

![Image](https://via.placeholder.com/150)

Figure 2.10 Flow stress as a function of temperature for a non-traditional bainite (NTB) steel with composition 0.34C, 1.21Mn, 0.66Si, 0.1Ni, 0.1Cr, 0.19Mo, 0.09V, 0.02Ti, 0.01N (wt pct). The microstructure consists of elongated ferrite grains with martensite-austenite islands. Samples were tested at an engineering strain rate of $10^{-4}$ s$^{-1}$ [26].

Figure 2.11 shows the results of tensile strength and ductility as a function of strain rate from the research of Okamoto et al. [40] on a martensitic steel tested at 150 °C. Serrated flow was observed from
At the lowest strain rate condition, continuous plastic deformation was observed (i.e. no DSA); however, there was an increase in tensile strength and a decrease in ductility compared to the higher strain rate conditions. Dynamic precipitation was proposed as a possible phenomenon to explain the increase in tensile strength and decrease in ductility observed. Okamoto et al. [40] hypothesized that dynamic precipitation requires high dislocation densities, low strain rates and elevated temperatures.

The research from Richards [26] and Okamoto et al. [40] indicated that dynamic precipitation potentially occurred at slightly higher temperatures and/or lower strain rates than the DSA regime and resulted in reduced ductilities (forming maxima in elongation measurements as a function of temperature and/or strain rate), increased flow strengths, and negative strain rate sensitivities.

![Strain rate dependence of tensile strength and total elongation](image)

Figure 2.11 Strain rate dependence of tensile strength and total elongation of a martensite sheet steel with composition of 0.14C, 1.48Mn, 0.27Si, 0.04Al, 0.004N, tested at a constant temperature of 150 °C. Figure adapted and redrawn from Okamoto et al. [40]. The DSA regime (based on serrated flow observations) is indicated by the two-directional arrow and the testing condition where dynamic precipitation was hypothesized is indicated with single arrows.

1.5 Characterizing Properties and Microstructures in X70 Steels During Elevated Temperature Plastic Deformation

The previous sections discussed literature X70 pipeline steels and mechanical behavior observed during plastic deformation around the DSA regime. The next sections provide background on synchrotron x-ray diffraction, stress relaxation, and internal friction testing, which were used in the present work to characterize microstructures, thermal and athermal components of the flow stress, and interstitial defects in the pipeline steels.
1.6 Synchrotron X-Ray Diffraction

High-energy x-rays have several useful characteristics that are desirable in studies of metals. High energy x-rays (e.g. 50-100 keV) have lower absorption cross-sections and penetrate much deeper into the material than low energy x-rays (e.g. 8 keV Cu k-α x-rays), which allows for bulk analysis of materials [75]. For reference, x-rays at the Advanced Photon Source (APS) can penetrate several millimeters of steel or aluminum and several hundred microns of high Z materials (e.g. gold or tungsten) [75]. Another useful characteristic of high energy x-rays is that the scattering process is simplified (compared to lab-scale equipment) and corrections for absorption, polarization, and anomalous dispersion are usually small or negligible [75]. Synchrotron x-ray wide angle x-ray scattering (WAXS) has proved to be effective for studying small volume fractions of phases in metals due to highly monochromatic beams and low background noise [76–80]. Figure 2.12 shows an example of the phase detection capabilities of synchrotron x-ray diffraction (at APS) where a WAXS line profile of a Grade 92 steel that consisted of a ferrite matrix with M_{23}C_{6} and Nb(C,N) precipitates was analyzed [77]. The highest intensity peak exhibited a signal to noise ratio of about 60. Even low intensity-high index precipitate peaks (e.g. M(662) in Figure 2.12) were detected. The low intensity peaks observed in the WAXS data were the result of diffraction of fine M_{23}C_{6} and Nb(C,N) particles in the steel microstructure. The size of the M_{23}C_{6} carbides detected in the diffraction pattern shown in Figure 2.12 were on the order of 1-2 μm and the σb(C,σ) were likely on the nm scale. The detection of low volume fraction/sub-micron size phases in steels made synchrotron WAXS experiments desirable to detect precipitates in the pipeline steels for the PhD work.

Figure 2.12 XRD line profile for a Grade 92 steel at room temperature. Diffraction peaks from α-Fe, M_{23}C_{6}, and Nb(C,N) phases are indexed. The intensity of the highest peak (α-Fe(110)) was about 6770 [77]. (Color image, the reader is referred to the .pdf version of this document).
1.7 Thermal and Athermal Components of Flow Stress

The flow stress of crystalline solids can be considered to consist of two components: an athermal component (internal stress) and a thermal component (effective stress) [81–83]. Figure 2.13 shows a schematic diagram of the energy barrier for the motion of a dislocation. For a dislocation to overcome the barrier (i.e. for plastic deformation to occur), a stress must be applied to account for both components. The athermal component is proportional to the shear modulus and the thermal component is more sensitively dependent on the temperature and strain rate. Activation volume (along with the effective stress) is a term related to the mechanical work done by the applied stress schematically shown in Figure 2.13 [84]. The activation volume magnitude can indicate the active dislocation structures. For example, deformation by Coble creep (a diffusion related deformation mechanism where atoms diffuse along grain boundaries under an applied stress), kink-pair motion, and forest dislocation interactions exhibit different activation volumes [84, 85].

Figure 2.14 shows two diagrams from Schoeck and Seeger [81] and Conrad [82], demonstrating the temperature dependence of flow stress in various materials. The thermal component of flow stress decreases with increasing temperature and approaches zero at a temperature of $T_0$. Effective stresses are associated with short range stress fields (i.e. interaction forces that act on a dislocation within a distance on the order of the Burgers vector of the dislocation line). For example, strengthening from lattice friction (Peierls stress) and solid solution strengthening are components of the effective stress. The athermal component of flow stress is thought to be constant at all temperatures and can be measured directly at high temperatures (i.e. when effective stress approaches zero). Internal stresses are associated with long range stress fields, which affect dislocation motion over a distance of multiple atom spacings up to on the order of the grain size. For example, components of the internal stress can include dislocation-dislocation interactions (e.g. pileups at grain boundaries) and precipitate strengthening [86].

Figure 2.14a is particularly relevant to the present work, as it outlines the DSA regime in iron with carbon and nitrogen interstitials and breaks down different parts of the effective stress regarding interstitial-dislocation interactions [81]. The yield stress at high temperatures (region C) is directly dependent on the internal stress. The internal stress is approximately constant at all temperatures, as discussed above. However, in region B, there is also an effective stress component originating from the Snoek effect (interstitial atom strengthening through locking solute atmospheres and dragging forces imparted on dislocations by carbon/nitrogen atoms) during dislocation movement. Region B was described to be approximately constant at temperatures up to region C. Region A was attributed to the tearing of dislocations away from carbon/nitrogen atmospheres (i.e. dislocations move during plastic deformation and the solutes are not mobile enough to diffuse to the dislocation cores, which effectively
describes a model of static strain aging [13]). Both the Snoek effect and static strain aging contribute to the effective stress in steels.

![Schematic diagram showing the energy barrier for the motion of a dislocation. ΔF is Helmholtz energy, τ* is effective stress, V* is an activation volume, and ΔG* is related to the internal stress.](image)

**Figure 2.13** Schematic diagram showing the energy barrier for the motion of a dislocation. ΔF is Helmholtz energy, τ* is effective stress, V* is an activation volume, and ΔG* is related to the internal stress.

![Schematic of the temperature dependence of the yield stress in iron containing carbon and nitrogen. Adapted from Schoeck and Seeger [81]. (b) Critical resolved shear stress vs. temperature for Zn and Cd single crystals. The athermal component (τ_a) is given by the relatively flat part of the curves above T_o [82].](image)

**Figure 2.14** (a) Schematic of the temperature dependence of the yield stress in iron containing carbon and nitrogen. Adapted from Schoeck and Seeger [81]. (b) Critical resolved shear stress vs. temperature for Zn and Cd single crystals. The athermal component (τ_a) is given by the relatively flat part of the curves above T_o [82].

1.7.1 Stress Relaxation Models for Measuring Activation Volume and Internal/Effective Stresses

Multiple testing techniques have been proposed for the measurement of internal/effective stresses and activation volumes [82]. Stress relaxation test methods have proven to be effective single specimen tests for measurements of all three parameters. Stress relaxation kinetics are dominated by the conversion
of elastic stress to plastic strain via thermally activated dislocation motion [83, 85]. By measuring the stress relaxation response of a material, inferences may be made as to the active dislocation structures (related to the activation volume) [82, 84, 85, 87–89] and the internal/effective stresses that contribute to flow stress [82, 83, 86, 89, 90].

In a stress relaxation test, the plastic deformation of a sample is paused while load-time data are collected. Key assumptions for stress relaxation models are: the mobile dislocation density is constant during the hold (i.e. the relaxation), the total strain (elastic plus plastic) during the hold is equal to zero, and the internal stress during the hold is constant. The result is an exponentially decaying load-time curve whose shape and magnitude are related to the internal/effective stress and activation volume. The general equation for stress relaxation is [87]

\[ \dot{\gamma} = -\frac{\tau}{G_{SM}} \]  \hspace{1cm} (2.2)

where \( \dot{\gamma} \) is the plastic shear strain rate during the hold, \( \tau \) is the applied shear stress, and \( G_{SM} \) is the combined sample/machine modulus. The activation volume (see Figure 2.13) is related to the thermally activated part of the strain rate given by

\[ \dot{\gamma} = \dot{\gamma}_0 \exp\left(\frac{-\Delta G_0 + \tau^*V^*}{kT}\right) \]  \hspace{1cm} (2.3)

where, \( \Delta G_0 \) is the activation energy, \( \tau^* \) is the effective stress, \( V^* \) is the effective activation volume (which can be expressed as \( V^* = kT \partial \ln \dot{\gamma} / \partial \tau^* \)), \( k \) is Boltzmann’s constant (1.381 x 10\(^{-23}\) J K\(^{-1}\)), and \( T \) is absolute temperature. Combining equations 2.2 and 2.3 results in the logarithmic expression

\[ \Delta \tau = \frac{kT}{\Omega V^*} \ln \left(1 + \frac{t}{C_r}\right) \]  \hspace{1cm} (2.4)

where \( \Delta \tau \) is the change in shear stress during relaxation, \( \Omega V^* \) is the apparent activation volume \( (V_{app}) \), \( C_r \) is a time constant related to relaxation plastic strain rate, and \( t \) is the relaxation time (\( t = 0 \) at the start of the relaxation, when the crosshead is paused). Apparent activation volume is related to the effective activation volume with the correction factor \( \Omega = (1 + K / G_{SM}) \times (1 + \beta) \), where \( K \) is the non-thermal strain hardening rate (which is a function of the relaxation conditions and sample stiffness) and \( \beta \) is an immobilization factor related to the dislocation density [87]. Non-linear least squares regression of Equation 2.3 with the stress relaxation curve \( \Delta \tau \ vs \ t \) yields a direct measurement of \( V_{app} \) and \( C_r \).
The apparent activation volume is considered to be the volume swept by dislocations during deformation and the microscopic mechanism governing the plastic deformation can be deduced from the activation volume and is a relative measure of the dislocation structure of a material [84, 85]. Activation volume measurements are typically normalized by the Burgers vector cubed. The magnitudes of activation volumes for a few deformation mechanisms are summarized in Table 2.1. Activation volume can be thought of as \( V^* = bdL \), where \( b \) is the Burgers vector of the dislocations, \( d \) is the obstacle size, and \( L \) is the characteristic distance between two obstacles. For fcc metals, forest dislocation interactions typically control dislocation motion. The distance between obstacles is related to the dislocation density \( \rho^{-1/2} \) and the obstacle size is approximately equal to the Burgers vector. A material with a dislocation density on the order of \( 10^{14} \text{ m}^{-2} \) results in an activation volume of about 400 \( \text{b}^3 \). For bcc metals, dislocation motion is typically controlled by the kink-pair mechanism [91]. For single kink migration, the distance between obstacles and the obstacle size are approximately equal to the Burgers vector, which results in an activation volume of approximately 1 \( \text{b}^3 \). For kink pair migration the activation volume is slightly larger and typical values range from 10-100 \( \text{b}^3 \). The literature [84, 85] also discusses the activation volume for solute atom interactions to be approximately 100 \( \text{b}^3 \) and Cobble creep mechanisms to be very small, on the order of 0.1-1 \( \text{b}^3 \).

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Activation Volume ( (V_{\text{app}} \times \text{b}^3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobble Creep</td>
<td>~0.1-1</td>
</tr>
<tr>
<td>Kink-Pair Motion (bcc metals)</td>
<td>~10-100</td>
</tr>
<tr>
<td>Solute Atom Interactions</td>
<td>~100</td>
</tr>
<tr>
<td>Forest Dislocation Interactions (fcc metals)</td>
<td>~100-1000</td>
</tr>
</tbody>
</table>

The development of activation volume with strain can be difficult to interpret for multi-phase materials, as multiple mechanisms may be active at any increment in strain [84]. Therefore, a complementary model was used with stress relaxation testing to measure internal and effective stresses [83, 86]. During the hold the applied crosshead speed \( \dot{x}_t \) is equal to zero

\[
\dot{x}_t = 0 = \dot{x}_e + \dot{x}_p
\]

where \( \dot{x}_e \) refers to the elastic part of the whole system (machine plus sample stiffness) and \( \dot{x}_p \) refers to the plastic part of the tensile specimen. The elastic and plastic parts are related to the Orowan relation.
\[ \dot{x}_e = \frac{1}{E_{SM}} \frac{dL}{dt} = \frac{A}{E_{SM}} \frac{d\sigma}{dt} \]

\[ \dot{x}_p = l\phi \rho b \bar{v} \]

where \( E_{SM} \) is the combined elastic modulus of the system (sample plus machine), \( L \) is the load, \( A \) is the cross-sectional area of the specimen, \( l \) is the gauge length of the specimen, \( \phi \) is a geometric factor, \( \rho \) is the mobile dislocation density, \( b \) is the Burgers vector, and \( \bar{v} \) is the average dislocation velocity which follows the equation

\[ \bar{v} = B(\sigma - \sigma_i)^{m^*} \]

where \( B \) is the average dislocation velocity at unit effective stress, \( \sigma \) is the applied stress, \( \sigma_i \) is the internal stress \( (\sigma - \sigma_i = \sigma^*) \), and \( m^* \) is the dislocation velocity-stress exponent (which is independent of applied stress or strain rate, but may depend on strain). Substituting equations 2.6, 2.7, and 2.8 into equation 2.5 results in the simplified expression

\[ \frac{d\sigma}{dt} = -\frac{E_{SM}}{A} l\phi \rho b B(\sigma - \sigma_i)^{m^*} = K'(\sigma - \sigma_i)^{m^*} \]

Integrating Equation 2.9 results in the expression used to analyze the stress relaxation curve

\[ \sigma^* = \sigma - \sigma_i = K(t + a)^{-n} \]

\[ n = 1/(m^* - 1) \]

\[ K = [(m^* - 1)K']^{-n} \]

\[ K' = \frac{E}{A} l\phi \rho b B \]

where \( a \) is an integration constant and \( n \) is essentially the creep exponent. Figure 2.15 shows the stress relaxation analysis (using Equations 2.10 through 2.13) of a LiF crystal studied by Gupta and Li [83]. The dislocation velocity stress exponent was first determined by measuring the derivative of the relaxation curve (i.e. the stress rate) at multiple times and performing a linear regression fit on a log-log scale. The integration constant \( (a) \) was assumed to be 0.4 s (Figure 2.15a). Equations 2.10 through 2.13 were then used to calculate internal/effective stresses during the relaxations at different points in the stress-strain curve (Figure 2.15b). Gupta and Li [83] observed approximately constant effective stress values as a function of strain and the internal stress values increased with increasing strain in the LiF crystal.
1.8 Internal Friction Testing

Internal friction is defined as the dissipation of mechanical energy connected with deviations from Hooke’s Law. In steels, internal friction is a measure of anelastic (time dependent) diffusion/formation of free interstitials (Snoek peak), trapped interstitials (Snoek-Ké-Koster peak), and dislocation kink formation ($\alpha$- and $\gamma$-Bordoni peaks) [92, 93]. Other material defects and phase transformations (not discussed in the present work) can contribute to internal friction; however, such species are not commonly associated with steels.

During an internal friction experiment, an elastic strain (usually on the order of $10^{-4}$) is applied and released continuously at a measurable temperature and loading frequency [92]. Upon unloading, only a portion of the elastic strain is recovered instantaneously. The remainder of the elastic strain undergoes anelastic relaxation (also known as the elastic after-effect), which is a time dependent phenomenon that results in the complete recovery of the remainder of the elastic strain. Snoek [94, 95] reported changes in the anelastic deformation properties as a function of temperature in iron containing small quantities of carbon and nitrogen interstitials. The anelastic effects were theorized to be due to the reconfiguration of interstitial atoms during elastic deformation. Figure 2.16 shows the torsional dampening response (quantified by the logarithmic decrement or phase lag in the measured vibration decay curve compared to the theoretical simple harmonic vibration decay curve [93]) due to interstitial nitrogen in iron. The peak
observed due to interstitial atoms has become known as the Snoek peak. The height of the Snoek peak is related to the total free interstitial concentration of the dampening source (e.g. carbon or nitrogen).

The specific model proposed by Snoek [93–95] for the internal friction relaxation due to carbon or nitrogen in α-iron (shown in Figure 2.16) is based upon the premise that these solute atoms occupy octahedral interstitial sites of the bcc lattice and diffuse during elastic deformation. The relaxation phenomena that contributes to the SKK peak is the same as the Snoek peak, except that the diffusivities of trapped interstitial atoms (at dislocations, grain boundaries, or phase boundaries) are different from free interstitial atoms, resulting in peaks at different temperature/frequency conditions. Octahedral sites are located at all positions midway along the edges of the two interpenetrating simple cubic lattices which together make up the bcc structure [13, 93]. The mechanism responsible for Bordoni relaxation is an anelastic response associated with the formation of dislocation kinks during elastic deformation [92].

Nowick and Berry [93] derived the dynamic response function for any single species contributing to internal friction by assuming they follow a diffusion based dampening response called the Debye relationship

\[
Q^{-1} = \frac{2Q_{\text{Max}(i)}^{-1}\tau_{0,i}e^{(Q_i/kT)(2\pi f)}}{1 + (2\pi f)^2\left[\tau_{0,i}e^{(Q_i/kT)}\right]^2} \tag{2.14}
\]

where \(Q^{-1}\) is the internal friction, \(Q_{\text{Max}(i)}^{-1}\) is the maximum dampening from species \(i\), \(\tau_{0,i}\) is the mean residence time of a defect at a site, \(Q_i\) is the activation energy of species \(i\), \(f\) is the vibrational frequency of the test, \(T\) is the absolute temperature of the test, and \(k\) is Boltzmann’s constant (8.617 x 10^\(-5\) eV/K). The species contributing to internal friction is assumed to have a discrete contribution to dampening (i.e. dampening from free carbon interstitials is independent of dampening from screw dislocation kink formation and free nitrogen interstitials, etc.). The dampening response is maximized when

\[
\tau_{0,i}e^{(Q_i/kT)(2\pi f)} = 1.0.
\]

At temperatures and/or frequencies above or below the optimum condition for dampening, there is diminished contribution of that defect species to internal friction, which results in peaks in the internal friction spectra related to specific defects (see Figure 2.16).

Activation energies and mean residence times in steels for Snoek, Snoek-Ké-Koster (SKK), and Bordoni peaks have been published in the literature and are summarized in Table 2.2 [92, 94–106]. The values included in Table 2.2 are averaged from values published in the literature. Nitrogen atoms have been shown to preferentially sit near manganese atoms in steels, which influences the diffusivity of interstitial nitrogen. Free nitrogen atoms, with no manganese atoms as nearest neighbors (the N\(_0\) Snoek peak), one manganese atom as a nearest neighbor (the N\(_1\) Snoek peak), and two manganese atoms as
nearest neighbors (the N\textsubscript{2} Snoek peak) exhibit individual Snoek peaks in the internal friction spectra [84, 107]. The activation energies of the Snoek peaks are different from each other, however the mean residence times for nitrogen interstitials are equivalent (as shown in Table 2.2).

![Figure 2.16](image)

Figure 2.16  Mechanical dampening reported by Snoek [95] for iron with small concentrations of nitrogen. Frequency of the experiment was 1 Hz.

<table>
<thead>
<tr>
<th>Peak</th>
<th>$Q_i$ (eV)</th>
<th>$\tau_o$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Snoek</td>
<td>0.875</td>
<td>$1.50 \times 10^{15}$</td>
</tr>
<tr>
<td>N\textsubscript{0}-Snoek</td>
<td>0.803</td>
<td>$2.04 \times 10^{15}$</td>
</tr>
<tr>
<td>N\textsubscript{1}-Snoek</td>
<td>0.841</td>
<td>$2.04 \times 10^{15}$</td>
</tr>
<tr>
<td>N\textsubscript{2}-Snoek</td>
<td>0.761</td>
<td>$2.04 \times 10^{15}$</td>
</tr>
<tr>
<td>SKK</td>
<td>1.50</td>
<td>$1.00 \times 10^{18}$</td>
</tr>
<tr>
<td>$\gamma$-Bordoni</td>
<td>0.750</td>
<td>$4.14 \times 10^{12}$</td>
</tr>
<tr>
<td>$\alpha$-Bordoni</td>
<td>0.070</td>
<td>$1.58 \times 10^{13}$</td>
</tr>
</tbody>
</table>

In the bcc crystal system (i.e. $\alpha$-iron), Snoek and SKK peaks exhibit anisotropic dampening when the crystal is elastically strained along different crystallographic orientations. Internal friction dampening is maximized when tensile and compressive stress are applied along the [100] direction and dampening is nullified (i.e. no dampening responses) when the tensile and compressive stresses are applied along the
[111] direction [92, 93]. Isotropic poly-crystals exhibit internal friction peaks in any orientation. However, sample orientation must be considered in heavily textured materials. In torsional pendulum internal friction experiments on a textured bcc material, sample orientations with the most [111] directions parallel to the torsional axis are optimal for maximum internal friction responses from interstitials. Grain size has also been shown to have an inverse relationship with interstitial dampening behavior (i.e. Snoek and SKK peak heights are lower in magnitude for small grained materials) [92].

1.8.1 Dynamic Strain Aging Studies using Internal Friction Analysis

Internal friction experiments have been performed to study static strain aging in the past [104], [107–110]. However, limited work has been done to study DSA with internal friction [30, 45, 111, 112]. Wagner et al. [30, 45, 111] related the Snoek and SKK peak heights with strengthening from DSA. Strengthening from DSA was shown to increase with increasing Snoek peak height (i.e. higher concentrations of carbon or nitrogen interstitials). Internal friction measurements from Wagner et al. were performed on the undeformed material and strengthening from DSA was equal to the equation:

\[(UTS_{\text{max}} - UTS_{\text{RT}})/UTS_{\text{RT}},\]

where \(UTS_{\text{max}}\) is the maximum ultimate tensile strength as a function of temperature and \(UTS_{\text{RT}}\) is the room temperature ultimate tensile strength. Karlsen et al. [112] performed internal friction experiments and dislocation substructure analysis on an AISI 316 austenitic stainless steel that exhibited DSA in the temperature range of 288-400 °C. Note, the internal friction peaks for fcc are different compared to bcc, as single free interstitials in fcc do not contribute to dampening [92].

Figure 2.17 summarizes the internal friction results from Karlsen et al. The lower temperature peaks (at approximately -50 and 100 °C) were a result of dislocation-point defect interactions and dislocation annihilation [113] and the higher temperature peak at approximately 350 °C is the Snoek-like relaxation (or Kelshtein-Rosin relaxation) [92]. Kelshtein-Rosin dampening undergoes a dislocation enhanced Snoek effect (i.e. the dampening is increased when interstitials are in the presence of dislocations).

Karlsen et al. [112] primarily focused on the high temperature, Kelshtein-Rosin peak in their analysis. Straining the material at low temperatures, outside the DSA regime, resulted in an increase in the Kelshtein-Rosin peak height. However, when DSA was active (at 288 and 400 °C) the Kelshtein-Rosin peak height approximately doubled compared to lower temperature deformation. Such an increase in the Kelshtein-Rosin peak height indicated that the number of interstitial atoms interacting with dislocations is greater when DSA is active compared to lower temperature conditions. Karlsen et al. [112] note that there are differences between the 288 and 400 °C behaviors, which have different serration morphologies, Kelshtein-Rosin peak heights, and dislocation substructures. The higher temperature condition exhibited both higher amplitude serrations in the stress strain-curve (Figure 2.17a) and the greatest increase in Kelshtein-Rosin peak height (Figure 2.17b). The data from Karlsen et al. imply that
greater Kelshtein-Rosin peak heights indicate greater strengthening from DSA. It may therefore be possible to relate serration morphologies combined with internal friction analysis to different levels of interstitial solid solution strengthening under various temperature-strain rate conditions within the DSA regime. Understanding dislocation-interstitial interactions in a bcc material can be done by studying how the Snoek and SKK peak heights change under different elevated temperature straining under various conditions within the DSA regime.

Figure 2.17 (a) Engineering stress strain curves of an AISI 316 stainless steel strained at various temperatures. The as-supplied condition indicates zero strain. DSA was observed in the 288 and 400 °C conditions. (b) Internal friction spectra of the same AISI 316 stainless steel. Test frequency was 1 Hz. Samples were pre-strained to 20 pct at indicated temperatures [112].
CHAPTER 3

EXPERIMENTAL DESIGN AND PROCEDURES

This chapter provides details on the experiments performed in the present work including: material selection, experimental procedures, and data analysis methods used to achieve the project objectives stated in Chapter 1. Tensile testing was used to strain the pipeline steels at various temperatures while using digital imaging correlation to map surface strains. Stress relaxation data were measured after pre-straining specimens to assess deformation mechanisms and internal/effective stresses. X-ray diffraction, synchrotron x-ray diffraction, transmission electron microscopy, and internal friction methods were used before and after tensile testing to study changes in phase and defect concentrations after straining at elevated temperatures.

1.9 Purpose of Project

The primary purpose of the present research was to characterize the elevated temperature mechanical properties of X70 line pipe steels in the range of 200-350 °C. Although DSA was shown to occur at approximately the same temperature/strain rate regime for all steels tested, the MS work [12] revealed deviations in mechanical behaviors of X70 steels at elevated temperatures just outside the DSA regime when compared to an X52 steel and data from the literature (details of which are discussed in Chapters 1 and 2). The goal of the PhD work was therefore oriented to identify and develop greater fundamental understandings of the metallurgical factors (including DSA) that influence mechanical behaviors at elevated temperatures in X70 steels.

1.10 Material Selection

The mechanical properties of three commercially produced X70 steels were characterized and compared to a control X52 steel in the MS thesis [12]. The steel referenced as X70 3.1Ti/N in the MS work (now referenced as X70) and the X52 steel were selected for research in the current project. The chosen X70 steel was selected because it exhibited the greatest strengthening around DSA conditions and at temperatures around 300 °C (outside the DSA regime). The X52 was selected due to its ferrite-pearlite microstructure (commonly studied in the DSA literature) as a control material to provide comparisons between X70 steels and the literature regarding mechanical behavior around the DSA regime. Figure 3.1 shows characteristic micrographs of the two steels studied. The X70 steel has a quasi-polygonal ferrite microstructure with martensite-austenite (MA) and austenite (A) microconstituents (examples of which are indicated in Figure 3.1). The X70 quasi-polygonal ferrite grains were finer than the X52 ferrite grains (note the scale differences in the micrographs). A detailed analysis of the X70 microstructure is included.
in Chapter 7. The X70 steel was provided by Essar Algoma Steel and was used in a previous study which includes details of the processing history [54, 114] (also refer to Section 9.4.1). The X52 steel was provided by SSAB and the processing conditions were proprietary.

Figure 3.1 Characteristic scanning electron micrographs of the (a) X70 and (b) X52 steels. Examples of ferrite (F), martensite-austenite (MA), austenite (A), and pearlite (P) constituents are identified. Images are oriented with the plate longitudinal and normal directions oriented horizontally and vertically respectively.

Table 3.1 shows the chemical compositions (in wt pct), plate thicknesses, and approximate grain sizes of the pipeline steels studied. Both steels had similar carbon concentrations of about 0.045 wt pct. The steels also had additions of manganese, aluminum, and microalloying elements (titanium, niobium, and vanadium), which have been shown to have significant effects on DSA responses to flow stress (see literature review section of the MS thesis [12]). Manganese holds nitrogen atoms in close association, limiting the diffusive jumps needed to pin dislocations and decreasing the strain aging response from nitrogen interstitials [19]. Aluminum and microalloying elements can remove interstitial carbon/nitrogen from the microstructure in the form of carbides/nitrides [13, 15, 17, 19, 24]. The X52 steel grain size is much larger than the X70 steel. Rodriguez [15] has shown that the slope of the Hall-Petch relationship changes and the maxima in strain hardening is greater for smaller grain materials when testing in the DSA regime.

Both steels have strong nitride forming elements as part of their chemical compositions. It was hypothesized in the MS work [12] that there was no free nitrogen in solution due to significant additions of titanium, vanadium, niobium, and aluminum. Table 3.2 shows partial chemical compositions for both steels in at pct and calculated equilibrium free nitrogen after the complete formation of selected nitrides at room temperature. Titanium is the strongest nitride forming element in both steels. The X70 steel has approximately a 1:1 Ti:N ratio (in at pct) and has almost no free nitrogen in solution after complete
formation of TiN. The X52 steel does not have enough titanium to remove nitrogen from solution alone. However, when all of the possible nitride forming elements are accounted for, both the X52 and X70 steels were unlikely to contain interstitial nitrogen. Internal friction analysis (discussed in Chapter 8) supported the hypothesis of both steels having no interstitial nitrogen in solution.

| Table 3.1 - Chemical Compositions (wt pct), Plate Thicknesses, and Grain Sizes of Line Pipe Steels |
|------------------|----------------|---|---|---|---|---|---|---|---|
| wt pct | Thickness (mm) | C | Mn | Si | Ni | Cr | Mo | Ti |
| X70 | 12.7 | 0.045 | 1.57 | 0.30 | 0.29 | 0.25 | 0.094 | 0.015 |
| X52 | 13.5 | 0.048 | 1.19 | 0.17 | 0.14 | 0.10 | 0.040 | 0.003 |

<table>
<thead>
<tr>
<th>wt pct</th>
<th>Nb</th>
<th>V</th>
<th>Al</th>
<th>N</th>
<th>S</th>
<th>P</th>
<th>Cu</th>
<th>B</th>
<th>GS (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X70</td>
<td>0.065</td>
<td>0.005</td>
<td>0.026</td>
<td>0.0049</td>
<td>0.0015</td>
<td>0.007</td>
<td>0.13</td>
<td>-</td>
<td>2.4</td>
</tr>
<tr>
<td>X52</td>
<td>0.001</td>
<td>0.046</td>
<td>0.035</td>
<td>0.0109</td>
<td>0.0034</td>
<td>0.010</td>
<td>0.28</td>
<td>0.0002</td>
<td>16</td>
</tr>
</tbody>
</table>

| Table 3.2 - Partial Chemical Compositions (at pct) of Line Pipe Steels and Equilibrium Free Nitrogen after Select Nitride Formation |
|------------------|------------------|----------------|---|---|---|---|---|---|---|---|---|---|---|
| Chemical Composition (at pct) | Free N Remaining (at pct) |
| Steel | N | Ti | Nb | V | Al | TiN | (Ti, Nb, V)N |
| X70 | 0.0194 | 0.018 | 0.039 | 0.005 | 0.054 | 0.001 | -0.043 |
| X52 | 0.0433 | 0.004 | 0.001 | 0.050 | 0.072 | 0.033 | -0.020 |

1.11 Methodology of Experiments

The experimentation for the PhD work was designed to study measurable changes in properties/behavior after or during (in situ) straining at elevated temperatures. The primary temperatures of interest were broken down into three categories: room temperature (25 °C), DSA temperatures (100-250 °C), and high temperatures (around 300 °C), as different behaviors were anticipated in the three zones. Engineering strain and localized deformation behaviors were measured in situ using DIC. Interrupted strain, stress relaxation tests were performed during tensile deformation to assess changes in activation volume and internal/effective stresses with strain and temperature. As-received and pre-strained materials were studied with electron microscopy (scanning and transmission), x-ray diffraction (lab-scale at Colorado School of Mines, and WAXS at Argonne National Laboratory and the Cornell High Energy Synchrotron Source), and internal friction to assess microstructural, phase, and defect concentration changes after deformation. The results obtained from DIC, stress relaxation, microscopy, x-ray diffraction, and internal friction were paired with mechanical property results from the MS work (see Chapter 1) to achieve greater fundamental understandings of DSA and to characterize the subjective behavior of X70 steels during straining around 300 °C.

Two sample geometries were used for elevated temperature deformation in all experiments. Figure 3.2 shows machining drawings for both standard tensile and internal friction geometries. The
round sample geometry (standard) was used for elevated temperature tensile testing. Standard geometry follows Japanese Industrial Standards [115] and was machined with traditional machining methods. The flat sample geometry was the geometry designed for the CSM torsional pendulum and was machined with wire electrical discharge machining (EDM) for any surface adjacent to the gauge length.

Figure 3.2 (a) Round test sample geometry for elevated temperature tensile testing used in the MS thesis [12] and previous studies at the ASPPRC [116–118]. (b) Internal friction sample geometry. (c) Plate orientation schematic for reference to how the internal friction samples were oriented in the as-received plates. The round tensile samples were also machined with tensile axis parallel to the rolling direction.
Tensile samples for both materials were oriented in the longitudinal direction (with the rolling direction parallel to the tensile/torsion axis). The orientation of the internal friction samples was selected based on texture information from Al-Jabr’s work [54] on the same X70 steel used in the current study. It was concluded that a significant number of grains were oriented with [111] directions parallel to the rolling direction, which was the ideal orientation for torsional pendulum internal friction measurements (see Section 2.7 for anisotropic interstitial dampening behaviors in bcc metals). Fracture surface analysis of X52 tensile specimens indicated nearly isotropic grains (where anisotropy was evident in the X70 steel fracture surfaces [46]) and it was assumed that sample orientation for the X52 steel would be independent of friction measurements. This assumption was based on the fact that a material with isotropic grains will theoretically exhibit the same internal friction dampening responses from interstitials at all sample orientations.

1.12 Elevated Temperature Tensile Deformation

Tensile deformation was performed on an 89 kN (20,000 lb) Instru-Met screw driven electromechanical tensile frame. High temperature grip inserts were machined from Inconel® 718 and aged to peak hardness for high temperature performance and creep resistance [116–118]. Threaded grips (½ in-13 female thread to match standard tensile specimens), designed to slide into the grip inserts at testing temperature, were machined from A2 tool steel and Inconel® alloy HX (a high temperature nickel alloy). Additional fixturing was used to strain internal friction samples. The internal friction grips threaded into the standard grips so minimal change was needed for the test setup. The selection of the test frame and grip configuration produced a rigid test system that optimized the detection of serrations during DSA.

Sample temperature was maintained with an ATS 3210 clamshell furnace with associated ATS 3XWatlow/3XSSR temperature controller. The three/zone clamshell furnace is capable of heating at a maximum rate of 1200 °C/h to a peak temperature of 1200 °C. Type K thermocouples were used to provide the necessary feedback to the control system to ensure uniform heating within the furnace, as well as to monitor tensile specimen temperature during deformation. The sample thermocouple was spot-welded to the surface of the tensile specimen near the fillet for the standard samples and wrapped around the gauge length for internal friction samples (to avoid any type of damage to the gauge length). Table 3.3 shows the temperature settings for each of the three zones on the clamshell furnace used to achieve each desired testing temperature for both sample geometries. The target temperature was calibrated using samples with multiple thermocouples spot-welded along the gauge lengths. After testing, uniform sample temperature could also qualitatively be observed by uniform sample oxide color along the gauge length. The allowable temperature variation across the tensile specimen was ±2 °C during the calibration.
Sample displacement was measured using one of two methods. The first was with a modified MTS 632.51C-71 elevated temperature extensometer with a gauge length of 20.96 mm (0.825 in). The second was digital image correlation (DIC). Only one method could be used at elevated temperatures because both methods utilized a single extensometer/view port located at the front of the clamshell furnace. Figure 3.3 shows photographs of the test setup on the Instru-Met frame with extensometer setup and example images through the view-port of the two sample geometries at 300 °C.

Table 3.3 - Furnace Zone Temperatures for Desired Tensile Temperatures for Standard and Internal Friction Geometries

<table>
<thead>
<tr>
<th>T.Target (°C)</th>
<th>T.Upper Zone (°C)</th>
<th>T.Middle Zone (°C)</th>
<th>T.Lower Zone (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>100</td>
<td>195</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>170</td>
<td>290</td>
</tr>
<tr>
<td>200</td>
<td>130</td>
<td>220</td>
<td>370</td>
</tr>
<tr>
<td>225</td>
<td>170</td>
<td>250</td>
<td>400</td>
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<tr>
<td>250</td>
<td>180</td>
<td>280</td>
<td>430</td>
</tr>
<tr>
<td>275</td>
<td>210</td>
<td>305</td>
<td>455</td>
</tr>
<tr>
<td>300</td>
<td>235</td>
<td>335</td>
<td>485</td>
</tr>
<tr>
<td>325</td>
<td>255</td>
<td>355</td>
<td>505</td>
</tr>
<tr>
<td>350</td>
<td>290</td>
<td>390</td>
<td>530</td>
</tr>
<tr>
<td>400</td>
<td>370</td>
<td>440</td>
<td>570</td>
</tr>
</tbody>
</table>

Tensile deformation was conducted in air at room temperature and in the temperature range of 100-400 °C, with engineering strain rates ranging from 1.67 × 10^{-4} to 1.67 × 10^{-3} s\(^{-1}\) (referred to as 10^{-4} and 10^{-3} s\(^{-1}\) when referencing testing conditions). Engineering strain rates were calculated using

\[
\dot{\varepsilon} = \frac{v_c}{l_{eff}}
\]  

where \(\dot{\varepsilon}\) is the engineering strain rate, \(v_c\) is the crosshead velocity, \(l_{eff}\) is the specified gauge length of the tensile or internal friction specimen. Test specimens were loaded into the frame with a pre-heated furnace. A 445 N (100 lb) or 223 N (50 lb) load was applied to the standard and internal friction samples respectively to maintain alignment during specimen heating. Uniform temperature across the gauge length was achieved after approximately 20 min.

1.13 Digital Image Correlation

As mentioned in the previous section, DIC was used to map surface strain in situ during elevated temperature straining of X52 and X70 steels. Figure 3.4 shows a photograph of the two-dimensional (2-D) DIC equipment setup for elevated temperature tensile testing. An Allied Vision Technologies®
Manta camera was used with a 2.8-32 f/50 mm Schneider Kreuznach® manual lens. The program used to operate the camera was TQS Snap® and strain calculations were performed using the ARAMIS® software by GOM.

Figure 3.3 Elevated temperature tensile test setup. The frame with assembled furnace is shown on the right with the extensometer/DIC viewing port labeled. Images on the left show a standard sample in the Inconel® grip inserts with the MTS extensometer assembled and two views of speckled standard and internal friction samples at 300 °C. (Color image, the reader is referred to the .pdf version of this document).

Light was polarized using filters indicated in Figure 3.4 (one in front of the light source and one attached to the lens). The speckled sample was viewed through the extensometer port in the clamshell furnace. The maximum frame rate for analysis of the 2-D DIC camera was 1 Hz (note, the camera is capable of higher frame rates, but the TQS Snap® software, used to take images, limited the imaging framerate). For most of the DIC analysis, 1 Hz was used for the high strain rate condition (10^3 s^-1) and 0.1 Hz (10 s delay per image) was used for the low strain rate condition (10^4 s^-1). The different frame rates allowed for identical strain increments between images for both strain rate conditions in incremental strain analysis.

Figure 3.5 shows two photographs of a speckled sample taken with the 2-D DIC camera. The first image is of the unstrained sample and the second image is of a strained condition just prior to failure at a
temperature of 150 °C. Pairs of images, like what are shown in Figure 3.5, were used to make engineering strain measurements during mechanical deformation. A boron nitride spray was selected for the speckle pattern, due to its ability to adhere to the sample during deformation at elevated temperatures. The boron nitride spray was excellent for steels in the temperature range of 25-400 °C due to its color contrast between the spray and the metal at all testing temperatures. At different testing temperatures, the steel surface changed colors depending on the thickness of the oxide layer formation. The color change sequence was reported in previous publications [12, 46]. From 25-275 °C, boron nitride was bright white and had excellent contrast compared to the sample. At approximately 275-300 °C the boron nitride spray turned a gray color, but since the steel surface was a copper to blue color at these temperatures, there was still enough contrast for displacement calculations with DIC.

Figure 3.4 Photograph of the elevated temperature testing setup with 2-D macro DIC equipment. (Color image, the reader is referred to the .pdf version of this document)

All strain measurements with 2-D DIC in the present work were calculated using deformation along the tensile axis. Figure 3.5 shows that the depth of field with the 2-D DIC camera was large enough to focus on the entire gauge length of the circular cross-sectional geometry of the standard tensile specimen. To avoid errors in the 2D surface strain calculations on a 3-D sample, only strains parallel to the tensile axis were analyzed. It was assumed that the circular cross-sectional geometry of the standard samples had no adverse effect on the axial strain measurements.
Figure 3.5 Photographs of a speckled X52 tensile specimen taken with the DIC camera under polarized light. The top image is undeformed and the bottom image is just prior to failure. Sample temperature was 150 °C.

1.13.1 Serration Morphology and Incremental Strain Analysis Methodology

The primary purpose of DIC in the current work was to study localized plastic deformation during DSA and compare the behavior to serration morphologies. Figure 3.6 shows an example of how incremental strain analysis was performed and how the results are reported in Chapter 4. Engineering stress-time data were plotted to analyze serration morphology (note, serration morphology appearance was independent of stress-time or stress-strain was plotted). Incremental strain maps were generated at all time increments during the tensile test using the ARAMIS® software.

The incremental strain maps were useful to view the locations of the localized deformation. However, it was difficult to analyze the deformation band behaviors throughout the entire tensile test using the incremental strain maps. Therefore, a section was drawn parallel to the tensile axis (schematically indicated by the white dashed line in Figure 3.6) and incremental strain data along the section were plotted as a function of position along the gauge length. The results of the incremental strain sections were peaks where the location of the deformation band(s) were positioned along the gauge length at any given time increment. The height of the peak (max incremental strain) is equal to the average local strain rate (after dividing by time) of the deforming metal in the time increment. For example, the local strain rate of the plot in Figure 3.6 with a maximum incremental strain of approximately 0.4 at the time increment of 340-350 s was 0.04 s\(^{-1}\) (where engineering strain rate of the sample was 10\(^{-4}\) s\(^{-1}\)).

Three-dimensional contour plots (as shown in Figure 3.6b) of the incremental strain profiles were generated to analyze the localized deformation behaviors. The axes of the contour plots of the incremental
strain profiles were time (x-axis), relative position along the gauge length (y-axis), and incremental strain (z-axis). Relative position along the gauge length was used on the contour plots because of the constantly increasing distance between data points due to elongation of the sample during the test. The number of data points along each incremental strain profile was constant, which allowed the data to be configured into a matrix making the large quantity of data easy to handle. The number reported at the top of the contour plot is the conversion factor between relative position and actual position (in mm) at time equals zero. The top and bottom of the contour plots represent the start of the fillets in the tensile sample.

Figure 3.6 Example diagram of the procedure for relating localized deformation to serration morphology using incremental strain analysis. The (a) engineering stress-time plots were compared to the (d) incremental strain contour maps, which were generated from the (c) section data from the (b) incremental strain profiles. The sample shown was the X52 tested at 98 °C and 10^{-4} s^{-1}. Time increment for the DIC analysis was 0.1 Hz. Color in this image represents incremental strain values. Blue indicates approximately zero incremental strain and transitions to lighter colors (white, yellow, red) to indicate higher levels of incremental strain. Note, there is a difference between color scales for the incremental strain map and the 3D incremental section data plot. (Color image, the reader is referred to the .pdf version of this document)
The color scales on the contour plots were selected based on the statistical error in the DIC calculations. Figure 3.7 shows 30 plots generated from DIC analysis (both incremental, Figure 3.7a and engineering strain, Figure 3.7b calculations) of an undeformed sample (i.e. actual strain equals zero for all plots). The range (maximum strain minus minimum strain, indicated by the dashed lines) was selected to define the background noise/error of the analysis. For both incremental and engineering strain calculations, the range error was approximately 0.32 pct strain. All strains less than 0.32 pct strain were considered to be noise for the incremental strain analysis and were colored blue on the contour plots. The color changed from blue to white (and red at relatively high incremental strains) when a peak in incremental strain intensity was detected above the background error. Peaks in incremental strain intensities were associated with localized deformation in tensile samples.

![Incremental Strain Background/Error](a)

![Engineering Strain Background/Error](b)

**Figure 3.7** Error analysis for (a) incremental and (b) engineering strain calculations with DIC. Each plot contains n = 30 strain profiles from images taken of an undeformed sample (i.e. zero strain for all profiles).

Three different types of localized deformation behavior were observed in the contour plots of the incremental strain profiles (all of which are present in Figure 3.6). The three behaviors were based on
comparisons of the relative positions of the localized deformation on the gauge length throughout the tensile test. During plastic instability (i.e. necking), the relative location of the localized deformation on the gauge length was approximately constant (starting at approximately 1000 s in Figure 3.6). Localized deformation associated with YPE or DSA (i.e. Luders or deformation bands) was observed to either propagate or nucleate along the tensile specimen during the tensile test. Peaks in incremental strain intensity moved continuously along the gauge length during deformation band propagation, which resulted in the appearance of diagonal white/red “lines” on the contour maps (e.g. see behavior of incremental strain intensity locations between 180-290 s, 400-510 s or 730-910 s in Figure 3.6). Deformation band nucleation was related to discontinuities in the relative positions of the peaks in incremental strain on the contour plots (e.g. deformation band nucleation events were observed between 290-300 s, 390-400 s, 510-520 s, 710-720 s, and 720-730 s in Figure 3.6).

1.14 Stress Relaxation Testing

Stress relaxation testing was performed to measure activation volume and effective/internal stresses in the X52 and X70 steels at various temperatures and strains. Standard elevated temperature tensile samples were selected for the stress relaxation tests, and deformation for all tests was performed at an engineering strain rate of $10^{-4}$ s$^{-1}$. The elevated temperature tensile test setup discussed in Section 3.4 was used for stress relaxation testing. Engineering strains were measured at each relaxation by calculating the average strain across an engineering strain DIC profile of the sample gauge length. Engineering strain profiles were measured at the start of the hold ($t \approx 0$), 100 s into the hold, and 200 s into the hold (i.e. just prior to the time when the stress relaxation measurement was complete and deformation continued). Figure 3.8 shows an engineering stress-time curve of the stress relaxation tests and the subsequent DIC engineering strain profiles for each hold. The samples were strained until plastic deformation was detected in the load-displacement data, where the crosshead was paused, and the load-time data was recorded during the hold for 200 s. After each hold, deformation continued for 100 s (long enough for the sample to undergo steady state deformation) and the crosshead was paused again for 200 s. A total of eight relaxations were performed on each sample. Images were taken for DIC analysis at a rate of 0.1 Hz. Measured strain using DIC was constant during each hold (i.e. no detectable strain change occurred while the crosshead was paused). All the measurements for a single testing condition were therefore made on a single sample. It was assumed that the pause in strain for collection of the load data during stress relaxation at one increment of strain did not affect the subsequent data. Stress relaxations were also carried out past the point of instability in the X70 steels (X52 specimens exhibited uniform deformation for all relaxations). True stress calculations were based on the maximum strain measured from the engineering strain profile for relaxation curves generated past the point of instability (i.e. relaxations 6-8
in Figure 3.8b). Data from stress relaxation measurements taken past the point of instability were consistent with measurements obtained during uniform deformation and it was assumed that the diffuse necks observed in the pipeline steels did not adversely affect the stress relaxation results.

![X70 25 °C Stress Relaxation Test](image)

**Figure 3.8** (a) Engineering stress time curve of the X70 25 °C stress relaxation test. The crosshead was paused while collecting data eight times during straining to measure the stress relaxation response at various strains. (b) Engineering strain profiles (measured with DIC) at all eight hold positions. Each engineering strain profile plotted was measured at the start of the stress relaxation hold (i.e. t = 0).

A key assumption for stress relaxation testing for both activation volume and internal/effective stress models is that the mobile dislocation density remains constant during the hold. However, testing conditions within the DSA regime violate the assumption for constant mobile dislocation density, as interstitial atoms can diffuse and pin mobile dislocations during stress relaxation. Robinson and Shaw [17] also discussed stress relaxation of material away from deformation bands during DSA as a possible driving force for different serration types. Any testing condition with highly localized plastic deformation (i.e. YPE with Luders bands, or deformation bands with DSA) were therefore considered invalid because of the possibility of non-uniform levels of relaxation along the gauge length of the specimens. The X52 steel exhibited YPE at temperatures up to 250 °C. Stress relaxation data were taken after YPE for all relevant conditions. The DSA regimes for X70 and X52 steels were approximately 90-245 °C at $10^{-4}$ s$^{-1}$. Valid stress relaxation tests were obtained at 25 °C and temperatures greater than approximately 245 °C.
1.14.1 Activation Volume Measurements

Equation 2.4 was fit to the stress relaxation data using least squares regression to measure the apparent activation volume \( V_{app} \) and the time constant \( C_r \). Shear stresses were calculated assuming that \( \tau = \sigma/\sqrt{3} \) [84]. Plots of the change in shear stress vs time for each hold were used for the activation volume fit. Activation volumes were normalized by the Burgers vector cubed \( (b = 0.248 \, \text{nm}) \). Figure 3.9 shows an example of activation volume measurements from all eight relaxations of the tests performed on the X70 25 °C sample (shown in Figure 3.8). Time equals zero was the moment when the crosshead was stopped for each hold. Activation volumes varied with strain and were reported individually and time constants were approximately constant for each temperature condition. Least squares regression was performed using the OriginPro® non-linear curve fitting function.

1.14.2 Internal/Effective Stress Measurements

Equation 2.10 forms the basis for the internal and effective stress measurements. The integration constant \( C \) was assumed to be 0.5 (note, that multiple values were used and it was found that the integration constant had little influence on internal/effective stress values calculated). Previous studies [86, 90] have used least squares regression with Equation 2.10 to calculate internal/effective stresses using the internal stress, dislocation velocity-stress exponent \( m^* \), and the K values as parameters. In this study, there were often multiple solutions for the fit. Therefore, the analysis procedure used by Gupta and Li [83] was used to separate the parameters of Equation 2.10 for a more reliable analysis of data. The stress relaxation curves of true stress as a function of time were plotted. As was done with the activation volume model, time equals zero was the moment when the crosshead was paused. The dislocation velocity-stress exponent can be measured by calculating the derivative of the stress relaxation curve (true stress vs time) and plotting it as a function of time on a log-log scale. Figure 3.10 shows an example of how the dislocation velocity-stress exponent was calculated. The derivative of the curve was taken for at least 15 data points along the curve using the OriginPro® tangent function application. The stress relaxation curve was first fit with a B-spline curve and the derivative was measured at individual points (schematically shown for two data points on Figure 3.10a).

The plot of \( \log(d\sigma/dt) \) vs \( \log(t) \) was fit with a linear regression to determine the slope of the data. Gupta and Li [83] noted that the analysis method used to calculate the dislocation velocity-stress exponent is invalid if the plot shown in Figure 3.10b does not fit a linear regression well. The analysis method is also invalid for materials with a slope greater than -1.0, as the effective stresses measured for these values are negative. The equation to calculate the dislocation velocity-stress exponent \( m^* \) is

\[
m^* = \frac{\text{slope}}{(\text{slope} + 1)}
\]
where “slope” is the slope of the linear regression of $\log(d\sigma/dt)$ vs $\log(t)$ plot. After the dislocation velocity-stress exponent is calculated, the internal stress can directly be calculated with

$$\frac{(\sigma_1 - \sigma_t)}{(\sigma_2 - \sigma_t)} = \left(\frac{K}{t_1 + a}\right)^n = \left(\frac{t_1 + a}{t_2 + a}\right)^n$$

where $\sigma_1$ and $\sigma_2$ are true stresses at times $t_1$ and $t_2$ during the hold respectively, $\sigma_t$ is the internal stress, $a$ is the integration constant (0.5 in the current work), and $n$ is the creep exponent (related to $m^*$ by Equation 2.11).

Figure 3.9  
(a) Stress relaxation curves for activation volume measurements for the X70 25 °C condition. (b) Activation volume, normalized with the Burgers vector cubed as a function of engineering strain for the X70 25 °C condition. $C_r$ was reported as an average and the error was the 95 pct confidence interval of the eight measured values.

Any two stress/time values during the hold are valid to calculate the internal stress. Therefore, calculations of internal stresses were performed with every iteration of the data points used in the $m^*$ plots (on the order of approximately 60 internal stress measurements from Figure 3.10b). Errors for the internal stress measurements were determined as the range (maximum calculated internal stress minus minimum calculated internal stress). Figure 3.11 shows an example of a true stress-engineering strain plot comparing internal and effective stresses to the flow stress of the X70 steel tested at 25 °C. As noted in Figure 3.8, the sample exhibited plastic instability at engineering strains greater than 10 pct. Diffuse
necking was concluded to have a negligible effect on the results, as the data points that exhibited plastic instability were repeatable and statistically comparable to values measured at lower strains.

Figure 3.10  (a) True stress as a function of time at 6.53 pct engineering strain for an X70 stress relaxation curve at 25 °C. Dashed lines schematically indicate the derivative of the curve at the locations of the circles. (b) The derivative of the stress relaxation curve as a function of time (on a log-log scale). A linear regression was used to fit the data and the slope of the regression was used to calculate the dislocation velocity-stress exponent ($m^*$).

Figure 3.11  Example of a true stress vs engineering strain plot showing internal/effective stress data compared to the flow stress of the material at several strains. The data plotted are from the X70 steel tested at 25 °C. Error bars represent the range of internal stress values ($n \approx 60$) calculated for each relaxation curve.
1.15 X-Ray Diffraction

X-ray diffraction (XRD) and wide-angle x-ray scattering (WAXS) measurements were completed to study phase changes in the X52 and X70 steels after tensile deformation at various temperatures. Experiments were performed at Colorado School of Mines (CSM), the Advanced Photon Source (APS) at Argonne National Laboratory, and the Cornell High Energy Synchrotron Source (CHESS). Since testing was performed at multiple locations with different energy x-rays, the XRD data are plotted as d-spacing vs normalized intensity for all scans. Dislocation density analysis of diffraction data was completed using the modified Williamson-Hall method.

1.15.1 Laboratory X-Ray Diffraction

Laboratory XRD measurements were performed on coupons taken from the gauge lengths of tested tensile specimens strained at a rate of $10^{-4}$ s$^{-1}$. Coupons were sectioned as far away from the fracture surface as possible without cutting into the fillet of the tensile specimen. The tensile bars were sectioned normal to the tensile axis to make the coupons. Strain was assumed to be approximately equal to the uniform elongation reported in Chapter 1. Thicknesses of the coupons were approximately 2 mm. Strain was assumed to be approximately equal to the uniform elongation of each sample. Coupons were ground on silicon carbide paper to 1200 grit as a final grinding step. It was assumed that the grinding process did not affect phase identification or dislocation density results.

A Phillips X’Pert® diffractometer with Cr-Tube source was used for laboratory XRD testing. The Cr-Tube source has a wavelength of 0.228976 nm (5.4147 keV). The Cu-Tube source was avoided because Cu Kα-radiation fluoresces iron, leading the lower signal to noise ratios compared to the Cr source. The Cr-Tube source was operated at 30 kV and 55 mA. Scans were performed from 64-158.9° with a step size of 0.008°, 20 s dwell time, 1° convergence slit, and 1° soiler slit. The data were cleaned by removing the Kα$_2$ peaks with the HighScore® software package.

Sample coupons were slightly less than 6.35 mm in diameter (depending on specimen uniform elongation), which is a smaller surface area than the area of the x-ray beam. The size of the x-ray beam was measured with a fluorescent disk that emits visible light when exposed to the x-rays. Figure 3.12 shows the geometry of the 3.8 x 8.8 mm beam in the Phillips X’Pert® diffractometer. To account for the relatively small sample size and avoid erroneous data from sample holder, a “zero-diffraction” plate was placed under the samples for XRD measurements. The zero-diffraction plate is a highly polished piece of single crystal silicon plate that was cut to an extreme crystallographic angle to avoid diffraction in the range of the diffractometer. The result was very low background noise in the space surrounding the sample that was in contact with the x-ray beam.
1.15.2 Synchrotron Wide Angle X-Ray Scattering

Testing at APS was performed on the 1-ID beamline for simultaneous collection of WAXS and small angle x-ray scattering (SAXS) data. The test setup for measurements at the 1-ID beamline was discussed by Tippey [119] and Whitley [120]. The data were collected at an energy of 71.679 keV and a beam size of 100 x 100 $\mu$m$^2$. Coupons were cut from the gauge lengths of tested X70 tensile specimens. Coupon thicknesses were approximately 2 mm (an appropriate thickness for x-ray transmission through the steel at 71.676 keV) and were cut as far away from the fracture surface as possible without cutting into the fillet. Strains were assumed to be approximately the uniform elongation values of each tensile specimen. A 2 mm thick as-received coupon (prepared in the same orientation as the tensile coupons) was also prepared. For each coupon, five WAXS measurements were taken from random locations on the sample. Each frame took between 0.3 and 2.0 s.

Testing at CHESS was performed at the F2 beamline. The data were collected at an energy of 61.332 keV and the beam sizes were 100 x 100, 200 x 200, and 500 x 500 $\mu$m. The detector consisted of six panels arrayed in a 3x2 matrix (the spaces between six detectors were accounted for in the analysis of the diffraction rings). The frame rates of the detector were 10 and 100 Hz and measurements were performed for 1.0 s. Coupons were cut from the gauge lengths of tested X70 and X52 tensile specimens. Coupon thicknesses were approximately 1 mm (an appropriate thickness for x-ray transmission through the steel at 61.332 keV) and were cut as far away from the fracture surface as possible without cutting into the fillet. Coupon strains were measured using DIC. The exact position of each coupon was measured relatively from the location of the fracture surface and the engineering strain was measured from the same location along the samples engineering strain profile just prior to failure. Internal friction samples (which
were also 1 mm thick), strained to approximately 5.1 pct (measured with DIC), were also studied using WAXS at CHESS.

The initial WAXS data were output as 2-D intensity images where diffraction rings were observed. These data were converted to 1-D profiles by integrating over the 90° azimuthal range of the 2-D intensity rings. Tippey [119] performed the conversion of the 2-D data to 1-D line scans for the APS WAXS study and the author of the current work performed the conversions for the CHESS WAXS study. A python script, developed by D. Pagan at CHESS, was used in conjunction with HEXRD® (a free software developed by the scientists at CHESS for high energy x-ray diffraction analysis) to convert the CHESS 2-D data to the 1-D line scans. Line scans were initially converted to normalized intensity vs two-theta. However, since two different x-ray energies were used for WAXS testing, two-theta values were converted to d-spacings using the Bragg equation [58] for discussions in the present document. Two theta values and machine peak broadening parameters were calibrated using a ceria (CeO$_2$) standard for both APS and CHESS testing. Background radiation was also accounted for in the data analysis. Figure 3.13 shows an example of a 2-D pattern converted to a 1-D line scan from the CHESS study. The two vertical black lines and one horizontal line on the detector image of the diffraction rings are the spaces between the six detector panels (see note above). Zero intensity was observed near these locations. Line scans exhibited extremely low background noise, enabling the detection of very low intensity peaks.

Figure 3.14 shows an example of a WAXS line scan of the X70 as-received steel from APS and CHESS experiments. Due to large variations of peak intensities in WAXS measurements, normalized intensity was plotted on a log scale, so all peaks were visible. Peak d-spacing values for ferrite and austenite phases exhibited good repeatability and the background noise was very low for the two experiments. Low intensity peaks were observed in the APS experiments at relatively high d-spacing values that were not attributed to ferrite or austenite. However, the low intensity peaks observed in the APS study were not observed in the CHESS data. After discussions with scientists at CSM, CHESS, and APS, it was hypothesized that the beam at CHESS is less monochromatic than the beam at APS, which resulted in slight spreading of the diffracted beam which can mask the presence of very low intensity peaks. The low intensity peaks, observed in the APS data, were hypothesized to be carbides and nitrides in the steel matrix. Methods for peak identification are discussed in Section 3.7.3.

Note, SAXS data (from APS) indicated that precipitates were detected in the X70 steel. However, after discussions with Ilavsky [121], it was determined that a larger Q-space, outside the capabilities of the 1-ID beamline setup used, was needed to perform accurate volume fraction and morphology analysis of the carbides/nitrides detected with SAXS. Therefore, SAXS analysis is not discussed in the present work.
1.15.3 X-Ray Diffraction Peak Identification

It was hypothesized that austenite, cementite, transition carbides, and MX carbides/nitrides (from microalloying element additions) were potentially present within the ferrite matrix. The HEXRD® program was used to simulate the d-spacing values of peaks from the hypothesized phases present. Table 3.4 shows the crystal structure, space group, and lattice parameter values used to simulate peak locations. Peaks observed in XRD and WAXS were compared to the theoretical locations of peaks for the hypothesized phases. Tables that include the simulated d-spacings for peaks in all the hypothesized phases are provided in Appendix A.

1.15.4 Dislocation Density Measurements with the Modified Williamson-Hall Analysis

The modified Williamson-Hall [122–126] analysis was used for semi-quantitative dislocation density measurements using diffraction peak broadening. Procedures from previous ASPPRC students [119, 127] were used for Williamson-Hall analysis in the present work. This sub-section briefly summarizes the analysis methods.

Diffraction peaks in polycrystalline systems have a finite width ($\beta$) which comprises the sum of three broadening terms: instrumental, strain, and grain size broadening. The instrumental term is quantified by using a standard material with very large grains and low amounts of strain. The grain size and strain terms are quantified by using the diffraction data from the sample and careful assumptions discussed below.
Figure 3.14  WAXS line scans (log normalized intensity vs d-spacing) comparing experiments performed at APS (black line) and CHESS (blue line). Ferrite and austenite peaks are indexed on the plot. All other peaks were hypothesized to be carbide/nitride peaks. *(Color image, the reader is referred to the .pdf version of this document)*

Table 3.4 - Crystal Structures and Lattice Parameters of Hypothesized Phases in Pipeline Steels

<table>
<thead>
<tr>
<th>Phase*</th>
<th>Crystal Structure</th>
<th>Space Group</th>
<th>Lattice Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe (Ferrite)</td>
<td>Body-Centered Cubic</td>
<td>No. 229</td>
<td>a = 2.867305</td>
</tr>
<tr>
<td>γ-Fe (Austenite)</td>
<td>Face-Centered Cubic</td>
<td>No. 225</td>
<td>a = 3.581350</td>
</tr>
<tr>
<td>Fe₃C (Cementite)</td>
<td>Orthorhombic</td>
<td>No. 62</td>
<td>a = 2.993</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 6.748</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 4.523</td>
</tr>
<tr>
<td>Fe₂₄C (ε-Carbide)</td>
<td>Hexagonal</td>
<td>No. 182</td>
<td>a = 2.993</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 4.624</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>γ = 120°</td>
</tr>
<tr>
<td>Fe₂C (η-Carbide)</td>
<td>Orthorhombic</td>
<td>No. 58</td>
<td>a = 4.704</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 4.318</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 2.830</td>
</tr>
<tr>
<td>Fe₃C₂ (Hägg Carbide)</td>
<td>Monoclinic</td>
<td>No. 15</td>
<td>a = 11.56770</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 4.571535</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 5.059484</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β = 97.7304°</td>
</tr>
<tr>
<td>NbN</td>
<td>Face-Centered Cubic</td>
<td>No. 225</td>
<td>a = 4.39</td>
</tr>
<tr>
<td>NbC</td>
<td>Face-Centered Cubic</td>
<td>No. 225</td>
<td>a = 4.47</td>
</tr>
<tr>
<td>TiN</td>
<td>Face-Centered Cubic</td>
<td>No. 225</td>
<td>a = 4.24</td>
</tr>
<tr>
<td>TiC</td>
<td>Face-Centered Cubic</td>
<td>No. 225</td>
<td>a = 4.33</td>
</tr>
</tbody>
</table>

* Parameters for the iron and iron carbide phases were provided in a private communication with Clarke and Clarke [128] in an unpublished document on transition carbides in 4340 steels. Parameters from MX phases (Nb,Ti(C,N)) were from Sourmail [129].
Kennett [127] accounted for instrumental broadening in an X-Pert® diffractometer using a Si standard (which was used in the present work in the CSM XRD results). After instrumental broadening is accounted for, grain size and strain broadening terms can be quantified individually. Williamson and Hall [122] proposed a method for the deconvolution of the grain size and strain broadening terms. The grain size term was first derived by Scherrer [130] as

$$
\beta_{GS} = \frac{K' \lambda}{D_{\mu} \cos \theta_B}
$$

where $$\beta_{GS}$$ is the broadening from grain size, $$D_{\mu}$$ is referred to as the “crystallite” size, $$K'$$ is a fitting constant (equal to 0.9 in the present study), $$\lambda$$ is the x-ray wavelength, and $$\theta_B$$ is the Bragg angle (in radians). It is hypothesized that the crystallite size is related to some small microstructural feature related to the grain size.

To accurately determine the strain term (related to the dislocation density), dislocation contrast factors must be applied to the Williamson-Hall analysis. The contrast factor is a fundamental parameter that determines the strength of line broadening of a specific peak caused by different types of dislocations [126]. Contrast factors in ferrite were calculated using the equations

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

$$
H^2 = \frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2}
$$

where $$\bar{C}_{hkl}$$ (also referred to as $$\bar{C}$$) is the average contrast factor of dislocations, $$\bar{C}_{h00}$$ is a constant obtained for cubic systems as a function of elastic constants $$C_{11}$$, $$C_{22}$$, and $$C_{44}$$ (see Forouzannehr et al. [131]), and $$q$$ is related to the nature of the dislocations (percentages of edge and screw present in the material). For a material that has 100 pct pure edge dislocations, $$q$$ is equal to 0.7 and for a material with 100 pct pure screw dislocations, $$q$$ is equal to 2.7.

The general equation for the Williamson-Hall analysis is

$$
\frac{\cos \theta_B (FWHM)}{\lambda} = \frac{0.9}{D_{\mu}} + \left[ \frac{\pi b^2 \rho}{2A} \right]^{1/2} \frac{2 \sin \theta_B}{\lambda} \bar{C}_{hkl}^{3/2}
$$

where $$FWHM$$ is the full-width at half maximum of the fitted peak (instrumental broadening subtracted), $$A$$ is a constant equal to 3.0, and $$b$$ is the Burgers vector (0.248 nm). Equation 3.7 can be simplified to
\[
\Delta K = B + m K C^{1/2}
\]

\[
\Delta K = \frac{\cos \theta_B (FWHM)}{\lambda}
\]

\[
K = \frac{2 \sin \theta_B}{\lambda}
\]

The dislocation density and crystallite size parameters are calculated by performing a linear regression of \(\Delta K vs K C^{1/2}\) (called a Williamson-Hall or W-H type plot). Figure 3.15 shows two examples of Williamson-Hall plots measured from the APS WAXS line scans of X70 in the as-received and 200 °C, 7 pct engineering strain conditions.

![Williamson-Hall Plots APS WAXS Testing](image)

**Figure 3.15** Example Williamson-Hall plots of X70 in the as-received and 200 °C 7 pct engineering strain conditions. Linear regressions were performed on the W-H plots and the slopes were related to the dislocation densities.

The slope \((m)\) from the linear regression is related to the dislocation density by

\[
\rho = \frac{2A m^2}{\pi b^2}
\]

and the intercept \((B)\) from the linear regression is related to crystallite size by

\[
D_p = \frac{0.9}{B}
\]
Only the dislocation density parameters are discussed in the present work. Calculated dislocation densities for the two linear regressions in Figure 3.15 were $4.01 \times 10^{14}$ and $4.22 \times 10^{14}$ m$^{-2}$ respectively for the as-received and strained conditions. Dislocation density measurements from strained samples were compared to the as-received conditions and the change in dislocation densities after straining at various temperatures was reported. Uncertainty analysis (i.e. the repeatability of measurements) associated with the modified Williamson-Hall dislocation density measurements required more testing, as only one WAXS line profile per condition was generated. Other sources of uncertainty in dislocation density measurements originated from the assumed values of parameters associated with the equations discussed above. Austenite decomposition in samples tested at relatively high temperatures (see Chapter 6) could also contribute to errors in peak broadening measurements.

1.16 Microstructure Analysis

Scanning and transmission electron microscopy (SEM and TEM) were performed as complementary techniques to WAXS for phase and dislocation analyses.

1.16.1 Electron Microscopy

Samples for SEM and TEM were obtained from the coupons used in the APS WAXS study. The coupons were mounted, polished to 1 μm, and etched with 2 pct nital to reveal the microstructure. TEM samples were machined using the focused ion beam (FIB) lift-out method used by previous ASPPRC students [127]. Prior to making TEM samples, SEM images of the microstructures were obtained.

An FEI Helios® 600i Dual Beam FIB was used for the SEM imaging and TEM sample machining. The FIB is equipped with a gallium ion beam and electron beam (for SEM imaging). TEM samples were taken from random locations in the X70 coupons strained at various temperatures. An SEM micrograph of the location of each TEM sample was recorded. The FIB lift-out geometry was selected over traditional TEM foils due to the reduced volume of material extracted, which results in smaller levels of magnetic interference in the TEM. Sample dimensions were approximately 20 x 10 x 0.1 μm which resulted in approximately 5-7 grains present in each lift-out.

An FEI Talos® F200X was used for TEM analysis to observe defects in the X70 quasi-polygonal ferrite grains. Selected area diffraction patterns (SADP) were used to view secondary phase diffraction spots within ferrite grains. Figure 3.16 shows example SADP and dark-field images using the low intensity diffraction spots to highlight precipitates and oxides in the ferrite matrix. Diffraction spots from iron oxide on the surface of the TEM foil and precipitates in the ferrite matrix were observed in the SADP. Spots hypothesized to be diffraction of carbides were used for dark-field imaging. Precipitates appear white in the dark-field image and the ferrite matrix is dark. It was assumed that only ferrite,
precipitates, and iron oxide were observed in the SADP (i.e. no austenite was present as extremely fine grains or films within the ferrite).

![SADP of the ferrite 111 zone 2-beam condition with 110 g-vector showing diffraction peaks from ferrite (α), carbides, and iron oxide in the X70 steel. (d) dark-field image using potential carbide diffraction spot indicated in (a) to highlight the precipitates (white spots) in the ferrite matrix (dark area).](image)

Figure 3.16  (a) SADP of the ferrite 111 zone 2-beam condition with 110 g-vector showing diffraction peaks from ferrite (α), carbides, and iron oxide in the X70 steel. (d) dark-field image using potential carbide diffraction spot indicated in (a) to highlight the precipitates (white spots) in the ferrite matrix (dark area). Images are from X70 steel in the as-received condition.

1.17 Torsional Pendulum Internal Friction Testing

Internal friction tests were performed to study carbon interstitial-dislocation interactions. A Vibran® torsional pendulum apparatus was used for internal friction measurements in the present work. The torsional pendulum is capable of heating from room temperature to a maximum safe temperature of 200 °C and the frequency range of the apparatus is 0.0001-10 Hz. A detailed user manual for performing room temperature variable frequency experiments was developed and is provided in Appendix B.

As discussed in Section 2.7, three types of peaks are theoretically observed in bcc systems: Snoek, Snoek-Ké-Koster (SKK), and Bordoni peaks. Activation energies and mean residence times (Table 2.2) were used with Equation 2.14 (the Debye equation) to calculate the theoretical temperatures and frequencies of the Snoek peaks for carbon and nitrogen, the SKK peak, and the γ-Bordoni peak (note that the α-Bordoni peak is observed at much greater temperatures and lower frequencies than the torsional pendulum is capable of testing). Figure 3.17 shows the theoretical peak locations for the C-Snoek, SKK and γ-Bordoni peaks. Note that the three N-Snoek peaks occur at slightly higher frequencies and lower
temperatures compared to the C-Snoek Peak. At room temperature, the torsional pendulum can detect the C-Snoek and γ-Bordoni peaks. However, the SKK peak occurs at frequencies far below the minimum frequency of the torsional pendulum. Elevated temperatures are required for direct measurements of the SKK peak.

For accurate internal friction spectra analysis, deconvolution of peaks and background signal is necessary. It was assumed that all peaks studied in the present work follow the Debye relationship and the background was subdivided into frequency, temperature, and machine components [107, 108]. Internal friction spectra were deconvoluted using non-linear least squares regression in OriginPro® with

\[ Q^{-1} = y_0 + AT + Be^{\left(D(T-E)\right)} + Ce^{\left(-d(2\pi f)\right)} + \sum_i \frac{2Q_{\text{Max}(i)}T_0ie^{(Q_i/kT)}(2\pi f)}{1 + (2\pi f)^2 \left[T_0ie^{(Q_i/kT)}\right]^2} \]  

where \( y_0, A, B, C, D, \) and \( E \) are background fitting parameters and the term in the summation is the Debye relationship discussed in Section 2.7. The background fitting term can be simplified when using constant frequency or constant temperature testing conditions. For example, a room temperature-variable frequency experiment causes the two temperature terms to be constants that can be accounted for by the \( y_0 \) parameter. One Debye term is required for each hypothesized peak. For example, if only interstitial carbon and screw dislocations are hypothesized to be present, one Debye term is used for each. But, if interstitial nitrogen is present, three additional Debye terms are required for the deconvolution.

In 2001, Al-Shalfan [108], used the Vibran® torsional pendulum at NIST for internal friction testing. Most of the testing conditions in Al-Shalfan’s study were room temperature-variable frequency experiments to study the C-Snoek peak after various heat treatments. Samples from Al-Shalfan’s work were used to verify that the torsional pendulum produced repeatable results equivalent to those obtained by Al-Shalfan [108] at NIST. Figure 3.18 shows the results of the validation experiment of the torsional pendulum. An internal friction spectrum of an unknown sample from Al-Shalfan’s work was heat treated at 720 °C for 60 s and tested at room temperature in the frequency range of 0.001-10 Hz. The measurement was repeated 12 times and the statistical error in the measurements (95 pct confidence intervals) are represented by the error bars. The measured spectra were compared to published data from Al-Shalfan’s work. The data comparison shows that the measured spectra for the unknown sample matched exactly to data published by Al-Shalfan [108]. Thus, it was concluded that the sample tested was the VL steel with chemical composition of 0.0045C, 0.21Mn, 0.021Si, 0.0039N, 0.015Ti, 0.088V (in wt pct). Digitized data from the VL steel is represented as open squares in Figure 3.18.
Figure 3.17  Theoretical locations of bcc Fe crystal internal friction peaks (calculated using the Debye relationship and parameters listed in Table 2.2) for (a) a room temperature-variable frequency experiment and (b) a 1 Hz-variable temperature experiment. The dashed line in (a) indicates the minimum frequency of the Vibran torsional pendulum for reference. The temperature scale in (b) is approximately the full safe temperature range of the torsional pendulum.

Figure 3.18  Room temperature-variable frequency internal friction spectra and deconvoluted C-Snoek and background curves of an unknown sample from Al-Shalfan’s [108] work annealed at 720°C for 60 s and compared to a digitized set of data from Al-Shalfan’s thesis heat treated with the same conditions. Error bars indicate the 95 pct confidence intervals of 12 measurements.
Preliminary verification experiments indicated that the torsional pendulum yields the most repeatable measurements at room temperature and with imposed frequencies greater than 0.001 Hz (i.e. the scatter in the data increased substantially when testing at elevated temperatures and very low frequencies). Upon heating, thermal expansion can cause misalignment in the system, resulting in increased levels of scatter in the data. Measurements at very low frequencies have increased scatter because the test durations take longer periods of time to complete and are therefore more susceptible to environmental effects (e.g. increased air vibrations and temperature fluctuations when the air-conditioning is turned on in the building). To obtain the most reliable results, room temperature-variable frequency experiments were performed to observe changes in the Snoek and γ-Bordoni peaks. Internal friction tests at room temperature were performed in the frequency range of 0.001-10 Hz with 41 different frequencies, evenly spaced on a log scale (see Figure 3.18 for an example). Tests completed after approximately 2 hours and automatically repeated until manually aborted. Most samples were run for approximately 24 hours (12 cycles). Average $Q^{-1}$ values were reported, and error was calculated as the 95 pct confidence interval of each testing condition. Occasionally, extreme (i.e. negative or excessively large) $Q^{-1}$ values were measured and were attributed to excessive dampening form isolated events in the testing environment. If a $Q^{-1}$ value was measured to be negative or more than one order of magnitude different from the average of all other tests at the same testing condition, the value was masked (i.e. excluded from the fit and error calculation) from the analysis. Less than 0.5 pct of measurements required masking.

Internal friction spectra were measured on X52 and X70 samples in the as-received and 3 pct strained conditions. Sample pre-strain temperatures were 25 °C (low temperature), 150 °C (low frequency serrations due to DSA), 200 °C (high frequency serrations due to DSA), and 300 °C (high temperature). Samples were stored in a deep freezer (approximately -20 °C) when not being strained or evaluated in the torsional pendulum to limit the mobility of interstitial atoms between measurements. After straining, samples were immediately cooled and returned to the freezer as fast as possible (usually less than 120 s). Strains greater than 3 pct were attempted. However, the elevated temperature fixturing was not optimized for the internal friction sample geometry and slight misalignment caused a bending moment on the grip sections during deformation. Misalignment in the internal friction specimens caused high levels of background noise in the internal friction measurements and the results were inconclusive. Alignment issues in the elevated temperature tensile setup for internal friction samples could be improved by machining new fixturing that uses pins within the holes in the grip section to apply the stress to the sample. The re-designed fixturing would allow for slight articulation of the sample on an additional axis to account for misalignment.
Attempts were made to measure the SKK peak with minor success. Tests were run at
temperatures between 100 and 200 °C and frequencies between 1 and 10 Hz. The samples were pre-
heated to 90 °C and alignment procedures were performed (see Appendix B) at temperature. The
relatively small temperature range was selected to reduce the misalignment in the torsional pendulum
caused by thermal expansion. The frequency range was selected to reduce the time of the experiments
since interstitial atoms are much more mobile at elevated temperatures. Figure 3.19 shows an example of
the SKK peak measurements in the as-received condition of the X70 steel. A peak was observed at
approximately the theoretical location of the SKK peak (see Figure 3.17). However, the limited
temperature-frequency space of the measurement complicated the deconvolution of the SKK peak from
background dampening. More work is required to optimize the torsional pendulum for use at elevated
temperatures.

Due to the complexities in the SKK peak measurements discussed above, only results from room
temperature-variable frequency experiments are discussed in the present study. It was assumed that there
was a negligible amount of decarburization during elevated temperature pre-straining resulting in a
constant total carbon concentration in the sample from the as-received condition to strained conditions.
Therefore, any changes in the Snoek peak height were assumed to result in a subsequent inverse change in
the SKK peak height given that WAXS and TEM phase analysis did not detect any significant phase
changes (e.g. the precipitation/dissolution of carbides or decomposition of austenite discussed in Chapter 6). Careful considerations of internal friction data were taken for testing conditions where phase changes were detected after straining.

1.18 Test Matrices for All Experiments

This section summarizes the target temperature and strain rate conditions for tensile testing with DIC, stress relaxation testing, XRD, WAXS, and torsional pendulum internal friction testing. Table 3.5 shows the tensile testing matrix for the DIC study (presented in Chapter 4). Both X52 and X70 samples were tested at $10^{-4}$ and $10^{-3}$ s$^{-1}$ at the temperatures indicated. Additional tensile testing experiments were performed without DIC to fully define the DSA regime based on serration morphologies (referenced as the serration morphology study). Temperatures were systematically selected to fully define the boundary conditions for serration morphologies at strain rates between $10^{-4}$ and $10^{-3}$ s$^{-1}$. Appendix C includes the load-time curves generated at various temperatures and strain rates that were part of the serration morphology study. Table 3.6 shows the testing matrices for stress relaxation, x-ray diffraction, WAXS testing at APS and CHESS, SEM/TEM, and torsional pendulum internal friction testing (presented in Chapters 5-8). Apart from stress relaxation experiments, which required plastic deformation for analysis, all characterization techniques compared data from the as-received and deformed conditions.

Table 3.5 - Tensile Testing Matrix (with DIC) for X52 and X70 steels.

<table>
<thead>
<tr>
<th>$\dot{\varepsilon}$ (s$^{-1}$)</th>
<th>25</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>225</th>
<th>250</th>
<th>275</th>
<th>300</th>
<th>325</th>
<th>350</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Table 3.6 - Testing Matrices for Characterization Experiments on X52 and X70 steels.

<table>
<thead>
<tr>
<th>Test Method</th>
<th>AR</th>
<th>25</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>225</th>
<th>250</th>
<th>275</th>
<th>300</th>
<th>325</th>
<th>350</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress Relaxation</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>X-Ray Diffraction (CSM)</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>WAXS (APS) – X70 Tensile Samples (e=UE)</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WAXS (CHESS) – Tensile (e=5 pct)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
</tr>
<tr>
<td>SEM/TEM – X70 Tensile Samples</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
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<tr>
<td>Internal Friction</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>
As-received, 25, 200, and 300 °C deformation temperatures had the highest analysis priorities because comparisons between room temperature (25 °C), DSA (200 °C), and high temperature (≥ 300 °C) conditions were desired. Synchrotron WAXS and SEM/TEM techniques were performed on strained tensile and internal friction samples and strains were approximately equal to the uniform elongation and 5 pct engineering strain respectively. Two additional WAXS experiments were performed at CHESS from the grip sections of the X70 300 and 350 °C experiments. Diffraction patterns from the grip sections were used to study the influence of temperature (without strain) on the secondary phases present.
Incremental strain DIC was used to study localized deformation behavior in both the X52 and X70 steels. From the MS results [12], plastic instability (i.e. necking), Luders bands (from static strain aging), and deformation bands (from DSA) were discussed as possible sources of localized deformation in the pipeline steels tested under testing conditions of interest. The goal of the DIC study was to relate stress-strain curve shape to observed deformation band behavior during DSA for steels. Note, serrated yielding and deformation band behaviors discussed in the following subsections are described using the naming system outlined by Rodriguez [15] (see Section 2.2.1). Classifications of serration morphologies in the present chapter are the authors best approximation based on examples/discussions from Rodriguez [15] and Robinson and Shaw [17]. Figure 4.1 shows the schematic of serration morphologies outlined by Rodriguez [15] that was presented in Section 2.2.1 and which is provided here for reference.

![Schematic stress-strain curves](image)

Figure 4.1  Schematic stress-strain curves demonstrating the different types of serrated yielding morphologies associated with DSA and the relative critical strain associated with each type. Figure was first published by Rodriguez [15] and was later re-drawn by Robinson and Shaw [17].

Rodriguez [15] discussed some observations of serration morphologies in terms of the critical strain required for serrated yielding ($\varepsilon_c$), which varied depending on the temperature-strain rate condition of the experiment. Discussions of the critical strain in the present study are only referenced qualitatively since flow curve morphologies were studied on engineering stress-time plots. Critical strains were
compared based on the time of the onset of serrated yielding for conditions tested at the same strain rate. A sample that had a relatively high critical strain exhibited the initiation of serrated yielding at a later time (and therefore larger strain) compared to another sample tested at the same strain rate.

Two characteristics were compared: stress-strain curve morphology and nucleation/propagation behavior of observed localized deformation bands. For example, a test that was described to exhibit Type A serrations indicated that the flow curve had similarities to what was schematically shown in Figure 4.1 (and Figure 2.6). Additionally, the deformation bands propagated unidirectionally along the gauge length, nucleating from one end of the gauge length to the other to continue deformation, as described by Rodriguez [15] and shown schematically in Figure 2.7.

1.19 Incremental Strain Analysis of Luders Bands, Uniform Deformation and Plastic Instability

Luders bands have been detected in many steel systems and have often been observed directly on the surface of polished tensile specimens [17]. Luders bands typically initiate at a stress concentrator (i.e. the fillet at one end of the gauge length) and propagate along the tensile specimen until the entire gauge length is traversed once. However, Luders bands can also initiate in the middle of the gauge length if misalignment in the tensile test introduces a bending moment on the sample or a geometry/machining defect causes a large enough stress concentrator. Yield point phenomena (YPE) is typically associated with Luders band propagation. At temperatures below the DSA regime, uniform deformation occurs in steels after Luders band propagation. Digital imaging correlation (DIC) was used to analyze Luders band behavior at room temperature to intermediate temperatures (up to 250 °C) in the X52 steel (note, the X70 steel did not exhibit YPE) to develop the analysis method for deformation bands associated with serrated yielding. Data from DIC were compared with the stress-time curves generated during tensile testing. Time was plotted instead of strain for easy comparisons of flow curve morphologies and DIC contour maps (see Section 3.5.1 for details on how contour plots were generated).

Localized deformation behaviors were compared to the serration morphologies by plotting the DIC contour maps and stress-time curves with aligned time axes. A vertical line drawn on the axes pair represents the incremental strain distribution along the gauge length at any point on the stress-time curve. Recall that white and red regions on the contour plots represent strain detected within the time increment used for the DIC analysis (1 and 10 s for $10^{-3}$ and $10^{-4}$ s$^{-1}$ respectively for most figures). Figure 4.2 shows the engineering stress-time curves and associated contour plots of the incremental strain profiles for two X52 specimens that exhibited Luders band propagation, followed by uniform deformation. Continuous propagation of the Luders bands from one end of the tensile specimen to the other was associated with the single continuous diagonal line of intensity on the contour profiles. Localized deformation initiated in the same time increment where YPE initiated on the flow curve. Propagation of the deformation bands ceased
at the opposite end of the gauge length in the same time increment where the horizontal YPE ended on the engineering stress-time plot. Uniform deformation was associated with the uniform light blue color observed from 260 to 1110 s on the room temperature sample (Figure 4.2a) and 25 to 97 s on the 97 °C sample (Figure 4.2b). Incremental strain measurements from uniform deformation were above the 0.32 pct background error (see Section 3.5.1) at the time increments used for the analysis.

Figure 4.2 Engineering stress-time and associated contour plots of the incremental strain profiles of the X52 steel tested at (a) 25 °C $10^{-4}$ s$^{-1}$, and (b) 97 °C $10^{-3}$ s$^{-1}$. Samples exhibited YPE and Luders band propagation followed by uniform deformation and then necking. (Color image, the reader is referred to the .pdf version of this document)

Some of the DIC contour plots exhibited parallel vertical lines that were considered as artifacts of the incremental strain analysis. Only some of the samples exhibited the vertical parallel lines which were hypothesized to be a result of the quality of the speckle pattern on the sample. The parallel vertical lines were observed as either blue (relatively low incremental strain intensity artifacts) or white (relatively high incremental strain intensity artifacts) lines on the contour plots. The blue and white vertical lines were often observed as a pair that occurred at the same relative position along the gauge length and one time increment apart from each other. For example, Figure 4.2b exhibited the vertical line artifacts that were hypothesized to be a result of poor speckle quality. A vertical blue line was observed at 93 s from 27-53 units of relative position along the gauge length and a vertical white line was observed at 94 s at
approximately the same position. The blue and white lines had average incremental strain values of approximately 0.005 and 0.33 pct respectively. The average incremental strain recorded at the location of the vertical line artifacts (i.e. the average of the incremental strain values at 93 and 94 s) was approximately 0.17 pct. The incremental strain intensity across the entire gauge length at times within the uniform deformation region was approximately 0.16 pct. Therefore, the average strain measured during uniform elongation was approximately the same as the average strain measured within the time increments where the vertical blue and white lines were observed. Some of the blue lines exhibited negative incremental strain values as well. Examples in Figure 4.2b where negative incremental strains were measured include at 32 s and a relative position of 70 (within the uniform elongation region) and 117 s and a relative position 11 (within the region of plastic instability but away from the neck where the average incremental strain was approximately zero). For all cases where the vertical line artifacts were observed, the average incremental strain between the blue and white vertical lines was approximately equal to the average incremental strain of the rest of that region of the contour plot.

Figure 4.2a shows an example of a sample that did not exhibit the vertical blue and white line artifacts in the contour plot. However, Figure 4.2a shows another artifact sometimes observed in the DIC strain analysis that resulted from the decohesion of some speckles from the sample. Red dots located at a relative position of 61 in Figure 4.2a between 1120 and 1340 s were a result of “holes” (i.e. regions on the sample where strain measurements were not possible) in the DIC analysis where the software lost track of the speckles in a very small region of the sample. It was hypothesized that speckles in the region where holes were observed fell off the sample during the experiment, which caused strain measurements in those regions to be impossible. The holes in the DIC analysis were typically only observed at relatively high strains.

Continuous yielding (i.e. initiation of plastic deformation without YPE), followed by uniform deformation was observed in the X70 steels at all temperatures and the X52 steel at high temperatures. Figure 4.3 shows the engineering stress-time curves with associated incremental strain contour plots for four examples of testing conditions that exhibited continuous yielding and uniform deformation. Figure 4.3a shows an example of a high temperature X52 sample that was tested outside the DSA regime at 284 °C and 10^{-3} s^{-1}. Approximately zero incremental strain was observed during elastic deformation, and at approximately 17 s uniform deformation was observed up to the point of instability at approximately 84 s. The criteria for instability was determined qualitatively by the approximate time of the onset of strain localization. Figure 4.3b shows an example of the X70 steel tested at room temperature and 10^{-3} s^{-1}. The flow curve morphology and contour map of the X70 25 °C 10^{-3} s^{-1} sample in Figure 4.3b had similar appearances to the X52 25 °C 10^{-4} s^{-1} sample from Figure 4.2a after Luders band propagation from YPE.
Figure 4.3 Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X52 284 °C 10^{-3} \text{s}^{-1}, (b) X70 25 °C 10^{-3} \text{s}^{-1}, (c) X70 101 °C 10^{-4} \text{s}^{-1}, and (d) X70 250 °C 10^{-4} \text{s}^{-1}. Samples exhibited uniform deformation and necking was the only detected form of localized deformation detected. (Color image, the reader is referred to the .pdf version of this document)
The X70 101 °C 10⁻⁴ s⁻¹ (Figure 4.3c) and X70 250 °C 10⁻⁴ s⁻¹ (Figure 4.3d) samples are examples of elevated temperature X70 experiments that were performed outside the DSA regime. Continuous plastic deformation was observed after elastic deformation and prior to plastic instability. Flow curve morphologies and contour plots for all figures presented in Figure 4.3 were equivalent to each other. Prior to yielding, no statistically significant incremental strain was detected (indicated by the blue region on the left side of the contour plots). Incremental strain values of approximately 0.2-0.4 were observed along the entire gauge length during plastic deformation up to the point of instability (maximum engineering stress).

All samples exhibited diffuse necking. Dieter [43] discusses the criteria for diffuse necking to be when the strain hardening rate ($d\sigma/d\varepsilon$) equals the true stress ($\sigma$) and is approximately equal to the maximum stress in an engineering stress-strain (or time) curve. Strain localization was observed to initiate at approximately the same time as the maximum engineering stress in Figures 4.1 and 4.2. At room temperature and temperatures above the DSA regime, diffuse necking was observed to initiate over a large percentage of the gauge length and slowly concentrate to a smaller relative area of the gauge length. The incremental strain intensity increased with increasing time during plastic instability. One interesting observation in necking occurred in the X70 101 °C 10⁻⁴ s⁻¹ sample (Figure 4.3c), which was close to the low temperature boundary of the DSA regime (the X52 steel exhibited DSA under the same testing conditions). Necking initiated over a smaller percentage of the gauge length in the X70 101 °C 10⁻⁴ s⁻¹ sample compared to all other samples that exhibited uniform deformation. The relative width of the localized deformation region at the onset of plastic instability was closer to what was observed in samples that exhibited DSA (see Section 4.1.2) than samples that exhibited uniform deformation. It was hypothesized that the more localized neck of the X70 101 °C 10⁻⁴ s⁻¹ sample was related to the proximity of testing conditions to the DSA regime.

1.20 Incremental Strain Analysis of Localized Deformation During Dynamic Strain Aging

This section is organized by introducing the types of serrations observed in the pipeline steels and the deformation band behaviors associated with different flow curve morphologies. The subsections are organized by the primary types of serrations observed at low strains (i.e. Types A, C, and D/E). Type B serrations were secondary serrations that are observed with primary serration types. Discussions with respect to testing conditions for different types of behaviors during DSA are discussed in Section 4.3 and the impact on mechanical properties in pipeline steels are included in Chapter 9.

As discussed in Sections 2.2 and 3.5.1, deformation bands can either propagate or nucleate along the gauge length of the tensile bar. Propagating deformation bands were hypothesized to appear like Luders bands, having a continuous diagonal line on the contour profiles (see Figure 4.2) and nucleation
events were hypothesized to result in discontinuities of the diagonal lines or individual peaks of incremental strain intensity on the contour profiles. Almost all testing conditions within the DSA regime for the X70 and X52 steels exhibited multiple types of serrations during deformation to failure. The low frequency serrations (Types A, D, and E) were either observed independently or with high frequency Type B serrations and most tests that exhibited either Types A, B or C at low strains transitioned to Type E serrations at high strains.

1.20.1 Type A Serration Morphologies and Deformation Band Behaviors

Type A deformation bands were classified by Rodriguez [15] as unidirectionally propagating deformation bands that nucleated from one end of the gauge length and propagated to the other to continue deformation. Serration morphologies associated with Type A behavior have relatively low load drop (or serration) frequencies compared to Types B or C. Figure 4.4 shows engineering stress-time and associated contour plots of the incremental strain profiles for samples that exhibited YPE/Luders bands, Type A (low strains), and Type E (high strains) serration and deformation band behaviors. Note, this subsection primarily includes discussions of Type A behavior. Type E behavior is discussed in Section 4.2.2.

Both X52 elevated temperature flow curves in Figure 4.4 exhibited distinct YPE that had a similar morphology to what was observed at temperatures below the DSA regime in the X52 steel (see Figure 4.2). The associated plastic deformation behavior was approximately equivalent to the lower temperature behaviors as well, with the propagation of deformation bands from one end of the sample to the other. Type A deformation behavior proceeded after YPE.

In Figure 4.1 (and Figure 2.6), Type A serrations exhibited distinct load drops periodically throughout the load curve with a relatively low frequency compared to Types B and C serrations [15]. The morphology of the Type A serrations observed in the pipeline steels in Figure 4.4 was slightly more complicated than what was depicted in Figure 4.1. While distinct load drops were observed at relatively low frequencies, the morphologies of the flow curves between the distinct load drops appeared more irregular than was expected based on results from Rodriguez [15], having a comparable appearance to the Type E serrations at higher strains.

The hypothesized Type A deformation band behavior shown in Figure 2.7 closely matches what was observed in the pipeline steels. In the DIC contour plots, Type A deformation bands form multiple continuous diagonal lines of incremental strain intensity with the same sign slope (i.e. propagation relatively up the gauge length resulted in a positive slope on the contour plots), with discontinuities (nucleation events) observed when the incremental strain peaks reach the end of the gauge length.
Figure 4.4  Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X52 98 °C $10^4$ s$^{-1}$, (b) X52 149 °C $10^3$ s$^{-1}$, and (c) X70 200 °C $10^3$ s$^{-1}$. Samples exhibited Luders bands with YPE (X52 only), Type A serrations with the discontinuous propagation of deformation bands at low strains, and Type E serrations with continuous propagation of deformation bands at high strains. (Color image, the reader is referred to the .pdf version of this document)
The Type A deformation band behaviors appeared very similar to Luders band propagation, however, there were distinct differences between the two phenomena. Luders bands exhibited higher magnitude incremental strains compared to Type A deformation bands. Luders bands, observed between 180-280 s in Figure 4.4a and 18-28 s in Figure 4.4b, exhibited incremental strains greater than approximately 0.8 pct (the red region on the color scale) and Type A deformation bands exhibited incremental strains of approximately 0.6 pct (the white region on the color scale). It was also possible for the direction of propagation to vary between Luders bands and Type A bands, as shown in Figure 4.4b. The diagonal line indicating Luders band propagation had a relatively negative slope and the Type A deformation bands had a relatively positive slope on the incremental strain contour plot.

Both X52 contour plots in Figure 4.4 exhibited two Type A nucleation events (at 395 and 521 s in Figure 4.4a and 35 and 46 s in Figure 4.4b) and the X70 contour plot in Figure 4.4c exhibited one nucleation event (at 36 s). Each of the nucleation events occurred at the same time increment as a distinct load drop in the flow curve. Therefore, the more irregular morphologies between load drops (of similar appearance to Type E serrations) were associated with the propagation of deformation bands.

The X52 and X70 steels exhibited different temperature-strain rate conditions for independent Type A serration and deformation behaviors. At $10^{-3}$ s$^{-1}$ the X52 and X70 steels exhibited Type A behavior at approximately 150 and 200 °C respectively. The X70 steel also exhibited half the number of Type A load drops compared to the X52 steel (i.e. Type A deformation bands propagated along the gauge length once in the X70 steel and twice in the X52 steel). The X70 steel exhibited a lower uniform elongation compared to the X52 steel (based on the time to instability since both tests were tested at the same strain rate). The relatively smaller independent Type A region in the X70 steel was hypothesized to be due to the lower uniform elongation compared to the X52 steel since the Type E regions occurred for approximately the same length of time for both materials.

1.20.2 Types D and E Serration Morphologies and Deformation Band Behaviors

At high strains in Figure 4.4, prior to plastic instability, both the X52 and X70 samples exhibited a transition from Type A to Type E serration morphologies (phenomenon shown schematically in Figure 4.1). The deformation band behavior observed in the contour plots transitioned from the unidirectional propagation of deformation bands with nucleation events at the ends of the gauge length to the continuous propagation of deformation bands up and down the gauge length. The maximum incremental strain associated with the Type E deformation bands was approximately equal to what was measured in the Type A deformation bands (approximately 0.6 pct at the equivalent time increments used). As the samples approached the point of plastic instability, the width of the localized deformation region increased, and necking initiated near the location of the last Type E deformation bands to form. Flow
curve morphologies past the point of mechanical instability were smooth for all samples and localized deformation within the neck was not detected.

Based on literature descriptions of localized deformation in materials that use substitutional atoms for DSA [15, 17], it was hypothesized that Types A and D exhibited approximately identical deformation band behaviors (see Section 2.2.1 and Figure 2.7). Figure 4.5a shows an engineering stress-time curve and associated contour plot of the incremental strain profile of an X70 sample that exhibited serration morphologies nearly identical to a plot identified with Type D from Rodriguez’s [15] work with 316 stainless steels tested at 450 °C. The Type D serrations exhibited a more rounded appearance than what was schematically shown in Figure 4.1. The deformation band behaviors associated with the Type D serrations were nearly identical to what was observed for Type E and propagated continuously up and down the gauge length. Changes in propagation direction occurred at the ends of the gauge length only and were associated with local minima in the flow curves. The hypothesis of similarities in deformation behavior between Types A and D (discussed above) was rejected based on the observed continuous deformation band propagation in the X70 149 °C 10^{-4} s^{-1} sample. It was concluded that Types D and E exhibit equivalent deformation behaviors.

Figure 4.5 Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X70 149 °C 10^{-4} s^{-1} and (b) X70 225 °C 10^{-4} s^{-1}. Samples exhibited independent Type D/E serrations with the continuous propagation of deformation bands. (Color image, the reader is referred to the .pdf version of this document)
Figure 4.5b shows another sample that exhibited Type D/E deformation band behavior at a higher temperature than what was shown in Figure 4.5a (near the upper bound of the DSA regime, which was approximately 240 °C at $10^{-4}$ s$^{-1}$; discussed in Section 4.4). The critical strain for serrated yielding ($\varepsilon_c$) was relatively high compared to the lower temperature sample. The times of the critical strains in Figure 4.5a and 4.5b are indicated by the vertical dotted lines. Since the strain rates were the same for both tests, a higher time of $\varepsilon_c$ was directly related to a relatively higher critical strain. Uniform deformation was observed up to 480 s, followed by Type D/E serrated yielding and continuous propagation deformation band behaviors. Plastic instability for both samples discussed in Figure 4.5 initiated in the same manner as what was discussed above for Figure 4.4.

### 1.2.0.3 The Influence of Aliasing Errors on Detecting Deformation Band Nucleation Associated with High Frequency Types B and C Serrations

Sections 4.2.1 and 4.2.2 discussed types of serration morphologies associated with the propagation of deformation bands (Types A, D, and E). Rodriguez [15] shows in Figure 4.1 that the flow curve morphologies associated with deformation band propagation exhibited relatively low load-drop frequencies compared to Types B and C serrations (associated with deformation band nucleation). Due to the relatively high load-drop frequencies associated with Types B and C serrations and the limitations on the frame rate of the DIC camera used, the influence of aliasing errors on the appearance of the incremental strain contour plots were investigated. Aliasing errors can occur when two sets of signals with different frequencies are compared. In the present study, the time increment of the DIC analysis was used to study deformation band nucleation events that were theoretically associated with the load-drop frequency [15]. Aliasing occurs when a system is measured at an insufficient sampling rate and can cause misinterpretation of the processed data. In the present study, aliasing errors affect the ability of the DIC analysis to detect nucleation events during relatively high frequency load-drops in the tensile curve.

Figure 4.6 shows the engineering stress-time curve and associated contour plots of the incremental strain profiles of an internal friction sample strained at the 200 °C $10^{-4}$ s$^{-1}$ testing condition. The sample exhibited Type A + B behavior (discussed in further detail in Section 4.2.4) and was tested with a DIC camera frame rate of 1 Hz, to study the Type B deformation band nucleation behavior. The frame rate used was selected because the imaging frequency was greater than the frequency of the serrations (approximately 0.77 to 0.59 Hz). The increased frame rate reduced aliasing errors and the maximum incremental strain from Type B deformation bands was still greater than the 0.32 pct threshold from the error analysis (higher frame rates in DIC analysis reduced the total incremental strain measured for each time increment).
Figure 4.6  Engineering stress-time and associated contour plots of the incremental strain profiles of X70 200 °C $10^{-4}$ s$^{-1}$ internal friction sample. A time increment of 1 Hz (approximately equal to the Type B serration frequency and 10x higher than what was used for other samples at the same strain rate) to attempt to detect individual deformation band nucleation. (a) Overall serration and deformation band behavior. (b-d) Higher magnifications of (a) showing deformation behaviors in different regions of the flow curve. Dashed lines in (d) indicate approximate time increments of the contour plot. Blue boxes relate (b-d) with (a) by showing the locations of the higher magnification plots relative to the overall experiment. (Color image, the reader is referred to the .pdf version of this document)
Figure 4.6a shows the overall behavior of the Type A + B deformation bands and Figure 4.6b-4.6d show data from the same experiment at higher magnifications. The blue boxes on the load time curves relate the images presented in Figure 4.6 to each other. The general deformation behavior was similar to the Type A behavior observed in Figure 4.3 at the lower DIC imaging framerate, with Type A deformation characteristics starting at 83 s (Type A nucleation event at 154 s) and a transition to Type E behavior at approximately 283 s, followed by necking.

The Type B serrations observed exhibited two different serration frequencies during plastic deformation. At lower strains the serration frequency was approximately 0.77 Hz (Figure 4.6b) and at higher strains (prior to Type E behavior) the serration frequency was approximately 0.59 Hz (Figure 4.6c). Figure 4.6d shows how deformation band nucleation was detected on a small scale in the incremental strain analysis. The vertical dashed lines overlaid on the flow curve indicate the approximate position of the time increments used for the DIC analysis relative to the serrations. In time increments where load drops were observed, statistically significant localized incremental strain peaks were detected (red on the color scale). The width of the peak (vertical axis on the contour plot) is theoretically the size of one deformation band. The localized incremental strain was approximately zero for time increments where the stress-time curve exhibited a straight line with positive slope (i.e. load drops were not captured). It was verified that the slopes of the linear portions of the serrations in the stress-strain curve were the same and approximately equal to the elastic modulus of the material. At time increments where approximately zero incremental strain was measured, discontinuities of the localized deformation on the contour plots were observed. Nucleation events were detected at locations adjacent to previous deformation bands during the Type B serrations and it was concluded that band nucleation occurred at every load drop in the flow curve. However, the overall deformation band behavior was constrained to follow Type A behavior (which was discussed further in Section 4.2.4).

Aliasing errors manifested in the DIC data as undetected nucleation events. Nucleation events were undetected in sections of the flow curve where at least one load drop occurred in back-to-back time increments. For example, 235.5-236.5 s and 236.5-237.5 s time increments (in Figure 4.6d) both exhibited load drops (and theoretically deformation band nucleation events), but continuous incremental strain intensity was observed in the contour plot from 235.5-237.5 s.

The differences in aliasing errors for detecting the nucleation events with different serration frequencies-to-time increment ratios are shown by comparing the number of nucleation events detected to the number of Type B serrations observed in Figure 4.6. For example, at a 0.77 Hz:1.0 Hz ratio (Figure 4.6b), 32 load drops on the flow curve and 8 discontinuities on the contour plot were observed from 85-125 s, which indicated that only one nucleation event in four serrations was detected. At a 0.59 Hz:1.0 Hz ratio (Figure 4.6c) 29 load drops on the flow curve and 21 discontinuities on the contour plot were
observed from 200-250 s, which indicated that approximately two nucleation events in three serrations were detected. However, the overall Type A behavior (i.e. deformation bands nucleating at the ends of previous bands to mimic the behavior of propagation) was accurately characterized regardless of the aliasing errors. It was hypothesized that 0.5 Hz:1.0 Hz ratio of serration frequency to DIC frame rate would efficiently detect the nucleation behavior of Type B serrations as every other time increment would detect a load drop.

The observations from the aliasing study indicated that the DIC time increments of 10 and 1 s for $10^{-4}$ and $10^{-3}$ s$^{-1}$ tests used in the main study were ineffective at detecting all of the deformation band nucleation events associated with high frequency serrations due to aliasing errors. However, the overall deformation band characteristics were unaffected by aliasing errors and it was possible to detect a fraction of deformation band nucleation events associated with relatively high frequency serrations compared to the time increments used for DIC analysis. The results from the aliasing study indicated that deformation band nucleation occurred at every load drop in stress-time curves with high frequency morphologies. Further discussions of high frequency serrations in the following sections are carried out with the assumption that load drops in the flow curve are related to deformation band nucleation events.

1.20.4 Types B and C Serration Morphologies and Deformation Band Behaviors

Types B and C serrations exhibit relatively high frequency load drops compared to Types A, D, and E. Rodriguez [15] discusses Type B and C serrations to consist of deformation band nucleation. Type B and C serrations discussed below were often difficult to distinguish. Serrations were classified as Type B if the magnitude of the load drops were relatively small and/or if the serrations were present with a low serration frequency type. Serrations were classified as Type C if the magnitude of the load drops were relatively large compared to other high serration frequency samples. Figure 4.1 shows that Type B serrations have relatively lower magnitude load drops compared to Type C. Type B serrations are also commonly observed as a secondary morphology with Types A or D. Type C serrations are typically observed independently from other types of serrations. Deformation bands from Type B behavior were described to rapidly nucleate at locations adjacent to previous deformation bands [15]. Renard et al. [68] classified Type C serrations to appear chaotically, discontinuously, and in a non-correlated (or random) way. Theoretically, each deformation band nucleation event was associated with one load drop in the flow curve for Types B and C serrations.

It was sometimes difficult to distinguish between independent Type B and C serration morphologies in the pipeline steel flow curves. Figure 4.7 and 4.8 show engineering stress-time curves and associated contour plots of the incremental strain profiles of four X70 samples that exhibited independent high frequency serrations. Samples shown in Figure 4.7a and 4.7b are duplicate X70 samples
tested at approximately the same temperature and strain rate (222 and 223 °C respectively at $10^{-3}$ s$^{-1}$) and show the overall behaviors of the experiments. Figure 4.7c and 4.7d are higher magnification images of Figure 4.7a and 4.7b respectively, focusing on the high frequency serration regions of the plots. Similarly, Figure 4.8a and 4.8b show two X70 samples that exhibited similar serration morphologies compared to each other. Figure 4.8c and 4.8d show higher magnification images of Figure 4.8a and 4.8b respectively, focusing on the serration regions of the plots. Only subtle differences in serration morphologies were observed between Figure 4.7 and 4.8. Specifically, the specimens presented in Figure 4.7 exhibited higher serration frequencies compared to Figure 4.8. Independent high frequency Type B/C serrations were observed at relatively low strains, followed by a transition to Type E serration morphologies at higher strains prior to plastic instability. Type C deformation bands were distinguished from Type E bands by the maximum incremental strain detected. Types C and E deformation bands exhibited incremental strains in the range of 0.5-0.8 pct and 0.4-0.6 pct respectively.

The average Type B/C serration frequency in Figure 4.7 was approximately 1.25 Hz for both samples. Since the serration frequency was near the frame rate of the camera (1.0 Hz for $10^{-3}$ s$^{-1}$ tests) only a fraction of the nucleation events were detected in the contour plots due to aliasing (i.e. nucleation of deformation bands adjacent to each other could appear as continuous propagation depending on the time of the nucleation event relevant to the time increment of the DIC analysis).

The deformation band behaviors of the high frequency serrations (more clearly shown in Figure 4.7c and 4.7d) for the two samples varied slightly compared to each other. The X70 222 °C $10^{-3}$ s$^{-1}$ sample appeared to follow Type B behavior, since all the deformation band nucleation events occurred near the locations of previous deformation bands except near the ends of the gauge lengths. The overall (macroscopic) appearance of the deformation behavior was similar to Type A behavior (see Figure 4.4). Deformation band nucleation behavior in the X70 223 °C $10^{-3}$ s$^{-1}$ sample (Figure 4.7d) appeared more random than the 222 °C sample. Most of the nucleation events detected were located adjacent to previous deformation bands. However, three instances of deformation band nucleation were detected near the center of the sample and away from previous deformation bands. For example, between 28 and 31 s, four load drops were associated with four incremental strain peaks (i.e. deformation bands) in the contour plots located at different positions along the gauge length. The first two deformation bands at 28 and 29 s nucleated adjacent to each other at relative positions of 21 and 10 units along the gauge length respectively (i.e. relatively moving down the tensile specimen). The next nucleation event at 30 s was located at a relative position of 34 units along the gauge length (near the center of the tensile specimen and relatively far away from the previous deformation band located at a relative position of 10 units along the gauge length). The other two instances of deformation bands nucleating away from previous deformation bands in Figure 4.7d were from 32 to 33 s and 36 to 37 s.
Figure 4.7 Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X70 222 °C $10^{-3}$ s$^{-1}$, (b) X70 223 °C $10^{-3}$ s$^{-1}$. (c) and (d) Higher magnifications of select areas of (a) and (b) respectively, focusing on deformation band behaviors of the high frequency (Type B/C) serrations. (Color image, the reader is referred to the .pdf version of this document)
Figure 4.8 Partial engineering stress-time and associated contour plots of the incremental strain profiles of (a) X70 200 °C $10^{-4}$ s$^{-1}$ and (b) X70 251 °C $10^{-3}$ s$^{-1}$. (c) and (d) Higher magnifications of select areas of (a) and (b) respectively, focusing on deformation band behaviors of the high frequency (Type B/C) serrations. (Color image, the reader is referred to the .pdf version of this document)
The samples shown in Figure 4.8 had a relatively larger critical strain (based on the time of the critical strain for samples tested at equivalent strain rates) for serrated yielding and exhibited fewer high frequency serrations compared to the relatively lower temperature samples shown in Figure 4.7. For example, the X70 251 °C $10^{-3}$ s\(^{-1}\) (Figure 4.8b) and X70 223 °C $10^{-3}$ s\(^{-1}\) (Figure 4.7b) specimens exhibited critical strains at 36 and 28 s respectively. Uniform deformation was detected up to the critical strain (schematically shown by the dashed lines between the uniform deformation and Type C regions in Figure 4.8c and 4.8d), followed by what was classified as Type C, then Type E serrations prior to plastic instability. Type C deformation bands in the X70 200 °C $10^{-4}$ s\(^{-1}\) (Figure 4.7a) appeared somewhat randomly along the gauge length of the tensile bar, where the X70 251 °C $10^{-3}$ s\(^{-1}\) (Figure 4.7b) generally followed Type E behavior (the nature of the nucleation behavior is addressed later in this chapter).

High frequency, Type B serrations were observed with Types A and D serrations in the pipeline steels. Figure 4.9 shows two samples that exhibited Type A + B behavior. Type A + B serrations typically occurred at greater temperatures and lower strain rates than independent Type A serrations. Type B serrations were observed in the yield point elongation region of X52 and at low strains in Figure 4.9a and only a few Type B serrations were observed in the higher temperature condition shown in Figure 4.9b. The low frequency portions of the serrations in the X52 samples that exhibited Type A + B behavior (i.e. the Type A portions) were different compared to lower temperature conditions with independent Type A serrations because necking initiated off of the Type A serrations and there was no detectable transition to Type E.

The X52 222 °C $10^{-3}$ s\(^{-1}\) (Figure 4.9a) sample exhibited a larger number of Type A nucleation events (i.e. nucleation from one end of the gauge length to the other) compared to the other X52 samples that exhibited either Types A or A + B behavior. However, the overall deformation band behaviors of the Type A + B samples were somewhat indistinguishable from the independent Type A behaviors (discussed in Figure 4.4) at the time increment used for the analysis due to aliasing errors, which prevented the detection of nucleation events (refer to Section 4.2.3). Aliasing errors were a result of the difference between the DIC camera frame rate (1 Hz) and the Type B serration frequency (2 Hz in Figure 4.9a). However, the analysis of the Type A + B serrations at smaller time increments in Figure 4.6 concluded that Type A + B deformation occurred as a result of the rapid nucleation of deformation bands and the locations of nucleation sites were constrained to follow Type A behavior. The results from Figure 4.6 and 4.9 closely matched the hypothesized Type A + B behavior shown schematically in Figure 2.7.

Figure 4.10 shows four examples of samples that exhibited Type D + B behavior. The overall deformation behavior of the X70 203 °C $10^{-3}$ s\(^{-1}\) sample (Figure 4.10a) was comparable to the behavior discussed with the X70 149 °C $10^{-4}$ s\(^{-1}\) (Figure 4.5a). However, the added Type B deformation bands suggested that deformation occurred due to band nucleation that was undetected due to aliasing errors.
The X52 samples in Figure 4.10b-4.10d exhibited YPE at yielding, independent Type B serrations at low strains, and then transitioned to Type E + B or independent Type E serrations at high strains prior to plastic instability.

![Graphs showing engineering stress-time and associated contour plots](image)

**Figure 4.9** Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X52 222 °C $10^{-3}$ s$^{-1}$ and (b) X52 252 °C $10^{-3}$ s$^{-1}$. Samples exhibited Type A + B serrations with primarily discontinuous propagation of deformation bands. Deformation behavior in the X70 sample (a) transitioned to Type E behavior at high strains. *(Color image, the reader is referred to the .pdf version of this document)*

Individual nucleation events in Figure 4.10b-4.10d were difficult to detect due to aliasing errors. Therefore, an additional sample that exhibited Type E + B behavior was analyzed at a higher DIC camera frame rate to reduce aliasing errors that resulted from the high frequency Type B serrations. Figure 4.11a shows the engineering stress-time and associated contour plots of the incremental strain profiles of the X52 151 °C $10^{-4}$ s$^{-1}$ sample analyzed at a DIC frame rate of 0.33 Hz. Figure 4.11b-4.11d show higher magnification images of different parts of the flow curve presented in Figure 4.11a. The blue boxes in Figure 4.11a relate all the higher magnification images in Figure 4.11b-4.11d to the overall data. The general morphology of the flow curve in Figure 4.11a was approximately equivalent to what was observed in the X52 samples discussed in Figure 4.10. Type B serrations were observed during YPE, independently at low strains, and Type D + B serrations were observed at high strains prior to plastic instability.
Figure 4.10  Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X70 203 °C $10^{-3}$ s$^{-1}$, (b) X52 199 °C $10^{-3}$ s$^{-1}$, (c) X52 210 °C $10^{-3}$ s$^{-1}$, and (d) X52 202 °C $10^{-4}$ s$^{-1}$. Samples exhibited Type D/E + B serrations with both nucleating and propagating deformation band behaviors. (Color image, the reader is referred to the .pdf version of this document)
Figure 4.11  Engineering stress-time and associated contour plots of the incremental strain profiles of X52 151 °C $10^{-4}$ s$^{-1}$. An image frequency of 0.33 Hz was used to attempt to detect individual deformation band nucleation. (a) Overall serration and deformation band behavior. (b-d) Higher magnifications of (a) showing deformation behaviors in different regions of the flow curve. (Color image, the reader is referred to the .pdf version of this document)
Figure 4.11b shows the YPE and independent Type B regions of the X52 151 °C 10⁻⁴ s⁻¹ sample. The appearance of Type B serrations in YPE influenced the Luders band behavior. At lower temperatures (Figure 4.2 and 4.3), Luders bands were observed to initiate at one end of the gauge length and propagate across the sample once, which resulted in a single continuous diagonal line of intensity on the incremental strain contour plots. At higher temperatures, where YPE was observed with Type B serrations, the Luders band behavior was more discontinuous. Luders bands exhibited somewhat random nucleation events that were associated with load drops from the Type B serrations. Maximum incremental strain intensities from Luders bands were still greater than what was observed from deformation bands associated with DSA.

Independent Type B serrations were observed in Figure 4.11b between approximately 228 and 287 s. Within the region of independent Type B serrations, deformation bands nucleated throughout the tensile sample somewhat randomly. However, the locations of the incremental strain peaks associated with the independent Type B serrations rarely appeared at the same relative position along the gauge length. The deformation band behavior during independent Type B serrations was therefore classified as quasi-random nucleation. The quasi-random deformation band nucleation observed in the region of independent Type B serrations (Figure 4.11b) was similar to what was observed with Type C behavior (Figure 4.7 and 4.8). However, serration frequency and corresponding frequency of nucleation events from Type B was greater than what was observed for Type C.

Deformation band behaviors were hypothesized to be influenced by local strain hardening. For example, the number of possible nucleation sites of Type C and independent Type B (which exhibited the quasi-random behavior) was therefore dependent on the distribution of local strain hardening along the gauge length. Deformation band nucleation was most favorable at locations where the lowest amounts of total local strain hardening occurred. During plastic deformation, the number of high potential nucleation sites decreased with time until the entire gauge length experienced approximately the same amount of total strain. Once total strain along the gauge length reached an approximately constant value, the likelihood of subsequent deformation band nucleation was equal at all points of the gauge length again.

Figure 4.11c and 4.11d show the deformation band behavior of regions in the X52 151 °C 10⁻⁴ s⁻¹ flow curve that exhibited Type D + B and independent Type D serrations. Similar to what was observed with Type A + B behavior, nucleation events were observed with Type B serrations. However, the overall behavior was somewhat indistinguishable from independent Type D serrations (i.e. the locations of the deformation bands moved up and down the gauge length, changing directions at the fillets). Therefore, the nucleation sites were constrained to nucleate adjacent to previous deformation bands to accommodate the Type D behavior. For example, Figure 4.11c exhibited Type D + B serrations from 300 to 361 s and 378 to 400 s. Distinct incremental strain peaks from deformation band nucleation events at locations adjacent to previous peaks were observed for all instances where load drops from Type B serrations were greater.
than approximately 3 MPa (nucleation events were undetected for relatively low magnitude load drops observed between 315 and 336 s in Figure 4.11c).

At higher strains (Figure 4.11d), local sections in the flow curve exhibited Type D + B nucleation near ends of the gauge lengths (and local minima in the flow curve) and Type D deformation band propagation near the center of the gauge length. For example, in Figure 4.11d, continuous diagonal lines of incremental strain intensity in the DIC contour plot were observed from 400 to 430 s and 461 to 497 s, and six Type B load drops corresponded with five distinctly noticeable incremental strain peaks related to the nucleation of deformation bands (one nucleation event was undetected due to aliasing errors).

1.20.5 Local Strain Rates During Dynamic Strain Aging

Engineering strain rates, calculated for tensile tests with Equation 3.1, represented the average strain rate across the gauge length during plastic deformation. Note, that specimens discussed in the current study were deformed at engineering strain rates of $1.67 \times 10^{-4}$ or $1.67 \times 10^{-3}$ s$^{-1}$, but for simplicity the samples were referenced as $10^{-4}$ and $10^{-3}$ s$^{-1}$, respectively (see Section 3.4). However, during YPE, DSA, and necking localized deformation was observed and the strain rate of the deforming material (i.e. in the Luders/deformation bands or neck) was theoretically much greater than the calculated engineering strain rate. Local strain rates during YPE and DSA were assessed by measuring the maximum incremental strains of Luders/deformation bands and neck in the DIC analysis (see Figure 3.6c for an example). Approximate local strain rates were calculated with the maximum incremental strain values using

$$\dot{\varepsilon}_{inc} = \frac{\text{Max Incremental Strain}}{\text{Time Increment} \times 100}$$  \hspace{1cm} (4.1)

where $\dot{\varepsilon}_{inc}$ was the approximate local strain rate. The approximate local strain rates were plotted as a function of time and compared to the engineering stress-time and incremental strain contour plots in this section. Figures in the following discussion are presented in the same format as other figures discussed in previous sections of this chapter, except the maximum local strain rates were overlaid on the engineering stress-time curves so flow curve morphologies and deformation band behaviors could be compared to changes in the maximum local strain rates.

Figure 4.12 and 4.13 show engineering stress-time, maximum local strain rate-time, and associated contour plots of the incremental strain profiles of selected X52 and X70 samples that exhibited different serration morphologies. The engineering strain rate used for each test was indicated by the dashed lines for reference. Samples presented in Figure 4.12 and 4.13 exhibited different serration morphologies and deformation behaviors, including YPE and uniform elongation (Figure 4.12a), Type A serrations (Figure 4.12b), Type B and B + D serrations (Figure 4.12c), relatively high critical strain
Type A serrations (Figure 4.12d), Type D serrations (Figure 4.13a), and Type C serrations (Figure 4.13b). It was assumed that other samples with the same classifications of serration morphologies and deformation band behaviors presented in previous sub-sections exhibited the local strain rate behaviors discussed with respect to the select samples presented in this sub-section.

The X52 25 °C $10^{-4}$ s$^{-1}$ (Figure 4.12a), X52 252 °C $10^{-3}$ s$^{-1}$ (Figure 4.12d), and X70 200 °C $10^{-4}$ s$^{-1}$ (Figure 4.13b) samples exhibited uniform plastic deformation during parts of tensile tests. The maximum local strain rates during uniform deformation were approximately equal to the engineering strain rates calculated for the tests. Thus, it was concluded that the strain rates detected with DIC were approximately equal to the target strain rates of the tensile tests.

Luders bands resulted in the highest measured local strain rates compared to all other types of localized deformation evaluated. Maximum local strain rates during Luders band propagation in the X52 25 °C $10^{-4}$ s$^{-1}$, X52 98 °C $10^{-4}$ s$^{-1}$, and X52 151 °C $10^{-4}$ s$^{-1}$ samples were typically greater than one order of magnitude higher than local strain rates detected during uniform deformation (using a 10 s time increment for the DIC analysis). The highest values of local strain rates during Luders band propagation were also greater than any local strain rates measured during DSA. All of the samples discussed in Figure 4.12 and 4.12 exhibited deformation band propagation in some form.

Values of maximum local strain rates during deformation band propagation were lower compared to local strain rates during Luders or nucleating type deformation bands. Figure 4.13a shows an X70 sample that exhibited continuous propagation (Type D) of deformation bands. The highest maximum local strain rate values, up to $7 \times 10^{-4}$ s$^{-1}$, were measured at low strains (290-500 s). At approximately 500 s, the maximum local strain rates decreased to approximately $4.5 \times 10^{-4}$ s$^{-1}$. At relatively low strains, local minima in the flow curve (at 360, 420, and 500 s) associated with deformation band propagation direction changes at the ends of the gauge lengths, resulting in decreases in the maximum measured local strain rates.

Samples that exhibited discontinuous propagation (Type A) of deformation bands (Figure 4.12b and 4.12d) exhibited slightly different local strain rate behaviors compared to samples that exhibited continuous propagation of deformation bands. In Figure 4.12b, local strain rates of approximately $5 \times 10^{-4}$ s$^{-1}$ were observed during deformation band propagation and $7 \times 10^{-4}$ to $1 \times 10^{-3}$ s$^{-1}$ (i.e. distinct peaks in local strain rate) were observed at times where distinct load drops and deformation band nucleation events occurred. Similar results were observed in Figure 4.12d, however increases in maximum local strain rates during Type A deformation band nucleation were less significant compared to deformation band propagation.
Figure 4.12 Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X52 25 °C $10^{-4}$ s$^{-1}$, (b) X52 98 °C $10^{-4}$ s$^{-1}$, (c) X52 151 °C $10^{-4}$ s$^{-1}$, and (d) X52 252 °C $10^{-3}$ s$^{-1}$. Measured maximum local strain rate was overlaid on the engineering stress-time curves and the dashed line indicates the engineering strain for reference. Plot legends indicate the time increment used for the local strain rate analysis. (Color image, the reader is referred to the .pdf version of this document)
Figure 4.13 Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X70 149 °C $10^{-4}$ s$^{-1}$ and (b) X70 200 °C $10^{-4}$ s$^{-1}$. Measured maximum local strain rate was overlaid on the engineering stress-time curves and the dashed line indicates the engineering strain for reference. Plot legends indicate the time increment used for the local strain rate analysis. (Color image, the reader is referred to the .pdf version of this document)

Maximum local strain rates measured for deformation band nucleation were more influenced by aliasing errors compared to deformation band propagation. However, deformation band nucleation (observed in Figure 4.12c and 4.12b) analyzed at 10 s time increments exhibited evidence of greater local strain rate values compared to deformation band propagation. The influence of aliasing errors on the measured local strain rate values was studied in the X52 151 °C $10^{-4}$ s$^{-1}$ sample in Figure 4.12c by plotting the measured local strain rates measured with time increments of 10 and 3 s on top of each other and comparing the magnitudes of the data. At high strains, where deformation band propagation was observed, the measured maximum local strain rate values were approximately the same for both time increments, which indicated that aliasing errors were small. However, aliasing errors were more substantial for sections of the flow curve with high frequency serrations, where values were approximately two times greater for the 3 s time increment analysis. Local strain rates up to $3 \times 10^{-3}$ s$^{-1}$ (approximately 18 times greater than the engineering strain rate) were observed in the discontinuous YPE region. The difference between local strain rates during deformation band nucleation and propagation were clearly observed at higher strains in Figure 4.12c (recall from Figure 4.11, where the X70 151 °C
10^4 s^-1 sample was first presented, that the serration morphologies changed from Type D + B to Type B when localized deformation was observed at the ends and center of the gauge length respectively). Peaks in local strain rate were observed at the same times as the high frequency serrations (at 432, 501, 585, and 681 s) associated with deformation band nucleation near the ends of the gauge length. It was concluded that deformation band nucleation resulted in greater local strain rates compared to deformation band propagation.

1.21 Classifications of Deformation Behaviors in Pipeline Steels

The serration type system discussed by Rodriguez [15] was only partially effective at characterizing the serrated yielding behavior of the X52 and X70 steels because flow curve morphologies were often more complex compared to materials where DSA was a result of substitutional atom/dislocation interactions. For example, it was often difficult to distinguish differences between independent Type B and Type C serration morphologies in the pipeline steels. Deformation band nucleation and propagation phenomena were analyzed with DIC and compared to the engineering stress-time curves to propose a serration classification system that fully defined the behaviors of the X52 and X70 steels. This section describes the proposed classification system and relates it to the serration type system used by Rodriguez [15].

Serration types were classified as either primary or secondary deformation bands. Primary bands formed the general flow curve shape and deformation behavior, and secondary bands could accompany primary bands in the form of high frequency load drops. For example, the X52 222 °C 10^3 s^-1 sample in Figure 4.9a exhibited Type A + B serrations between 37 and 66 s on the engineering stress-time curve. The larger periodic load drops (i.e. the Type A serrations most clearly visible at higher strains) formed the general shape of the flow curve and the higher frequency load drops (Type B serrations) were observed in-between the Type A serrations. The contour plot of the deformation band behavior indicated that deformation bands generally moved in one unique direction along the gauge length (relatively down the gauge length in this case) several times prior to plastic instability (Type A behavior). The presence of Type B serrations indicated that the deformation mechanism was constrained nucleation of deformation bands. The Type A serrations were considered the primary serrations and the Type B serrations were considered the secondary serrations.

Table 4.1 shows an outline of the proposed DSA deformation classification system related to the serration type system outlined by Rodriguez [15]. Primary deformation band behaviors, classified as discontinuous propagation (DP), continuous propagation (CP), and systematic nucleation (SN), were identified in the DIC contour plots of the incremental strain profiles discussed in Section 4.2. Secondary deformation band behaviors were classified as constrained nucleation (CN) and consisted of a change in
deformation mechanism from propagation to nucleation of deformation bands without changing the overall deformation path.

Discontinuous propagation of deformation bands were related to Type A behavior. Samples identified to exhibit DP behavior were discussed in Section 4.2.1 and were observed to initiate at one end of the gauge length, propagate to the other end of the gauge length, then nucleate at the initiation site to continue propagation in the same relative direction. Specimens with DP flow curve morphologies were also observed with secondary constrained nucleation behavior, where the deformation mechanism transitioned from unidirectional propagation to the nucleation of deformation bands. However, the overall deformation path was equivalent to independent DP behavior. Most testing conditions where DP behavior was observed transitioned to CP behavior at high strains. However, in the X52 steels tested near the upper boundary of the DSA regime, DP behavior was observed at relatively high strains following uniform deformation and preceded by plastic instability.

Table 4.1 - Preliminary Proposed Deformation Band Classification System

| Type A | Primary | Discontinuous Propagation (DP) | Unidirectional propagation of bands with nucleation events that occur when the deformation band reaches one end of the gauge length. |
| Type B (independent) and Type C | Primary | Systematic Nucleation (SN) | Quasi-random nucleation of bands that occur anywhere along gauge length at favorable sites based on the amount of local strain hardening at each potential nucleation site. |
| Types D or E | Primary | Continuous Propagation (CP) | Continuous propagation of bands that result in a relative direction change when the bands reach one end of the gauge length. |
| Type B (with A, D, or E) | Secondary | Constrained Nucleation (CN-DP or CN-CP) | Nucleation of bands where the potential nucleation sites are constrained to occur within the vicinity of the previous deformation band location. Overall behavior takes the form of the associated primary serration. |
Continuous propagation of deformation bands was related to Types D and E serrations and was observed in almost all tensile specimens that exhibited serrated yielding (excluding select X52 samples tested near the upper boundary of the DSA regime). Samples identified to exhibit CP behaviors were discussed in Section 4.2.2. Continuous propagation of deformation bands was either observed independently or at relatively high strains after uniform, DP, or SN deformation modes. Deformation bands observed in samples that exhibited CP deformation behaviors propagated up and down the gauge length continuously until plastic instability. Secondary CN deformation bands were also observed with CP behavior, which indicated a transition in deformation mechanism from propagating to nucleating deformation bands (similar to what was discussed with DP behavior above).

Systematic nucleation of deformation bands was related to Type C and independent Type B serrations (also discussed as having a relatively high serration frequency). Deformation behaviors with SN characteristics were discussed in Section 4.2.3 to quasi-randomly nucleate along the gauge length. The number of possible nucleation sites was dependent on the local strain hardening of previously deformed sites. Nucleation was most favorable at locations where the lowest amount of local strain hardening occurred. For example, the X70 223 °C 10^{-3} s^{-1} sample (Figure 4.7b and 4.7d) exhibited SN between 27 and 40 s on the engineering stress-time curve. Between the times of 27 and 34 s, seven independent nucleation events were detected on the DIC map at 1 s time increments. However, the deformation bands tended to nucleate next to previous deformation bands, which was hypothesized to be a result of a geometrical notch effect influencing the potential nucleation sites. Figure 4.14 shows the incremental strain profiles of the X70 223 °C 10^{-3} s^{-1} tensile sample from Figure 4.7b and 4.7d between 27 and 33 s. The position of maximum incremental strain was considered to be the location of the nucleation site. Between 27 and 32 s, nucleation events only occurred at locations away from previous nucleation sites, until the entire gauge length was approximately uniformly deformed. Deformation bands nucleated at approximately the same position as previous bands only after the tensile specimen achieved approximately uniform total strain along the entire gauge length.

1.22 Temperature and Strain Rate Dependence on Deformation Behavior

The serration maps discussed in Chapter 1 (see Figure 1.3) were used to discuss the general temperature/strain rate conditions for DSA. The DSA regime was indicated by the approximate upper and lower boundary conditions for transitions between serrated and uniform flow curve morphologies. The temperature range of interest for the MS work was 200-350 °C and only a few samples were run at temperatures below 200 °C to define the lower bound of the DSA regime. Therefore, only the upper bound of the DSA regime was well defined in the MS results. The results discussed in this section include
well defined temperature and strain rate conditions for DSA and indicate changes in deformation behaviors under varying testing conditions.

Figure 4.14 Strain profiles of select time increments of the X70 223 °C 10^{-3} s^{-1} tensile specimen (see also Figure 4.7b and d), showing systematic nucleation behavior of deformation bands between 27-33 s. The time increment for the analysis was 1 s for each profile.

Figure 4.15 shows detailed serration maps for the X52 and X70 steels in the strain rate range of 10^{-4}-2 x 10^{-3} s^{-1}. The serration maps outline the temperature-strain rate conditions for the DSA regime and indicate the testing conditions for the various types of localized serration/deformation behaviors discussed in the previous sections. Deformation behaviors were classified based on the observations from the DIC analysis discussed in the previous sections. However, the data presented in Figure 4.15 also include tests performed in the MS thesis and the serration morphology study (introduced in Chapter 3). Note, experiments in the serration morphology study were run at various temperatures and strain rates selected to systematically define the regions of the serration maps. Table 4.2 shows tabulated results of the serration morphology study, including the temperature-strain rate conditions where different serration morphologies were observed and compared to the DIC data presented in Section 4.2. The load-time curves of the samples included in the serration morphology study are included in Appendix E for reference. Stress-strain data from the MS thesis samples and load-time data from the serration morphology study were used to assess deformation behaviors of samples based on correlations between flow curve morphologies and deformation band behaviors discussed in Section 4.2.

The temperature range (at all strain rates) of the DSA regime was slightly greater for the X52 steel compared to the X70 steel. Most noticeably was that the lower boundary of the DSA regime occurred at lower temperatures in the X52 steel compared to the X70 steel. At 1.67 x 10^{-3} s^{-1} the lower boundary of the DSA regime was approximately 112 and 143 °C for the X52 and X70 steels respectively. It was hypothesized that nitrogen interstitial/dislocation interactions could be responsible for the
differences in the lower temperature boundary of the DSA regime. It was discussed in the materials selection (see Section 3.2) section that nitrogen atoms were only likely present as nitrides in both steels because of the relatively high concentrations of stable nitride forming elements. However, the X52 steel had relatively fewer strong nitride forming elements compared to the X70 steel, so it was possible for free nitrogen to be present in X52. Internal friction analysis was used to detect relative concentrations of free interstitial nitrogen and/or carbon atoms in both steels. However, the results were inconclusive in terms of the detection of interstitial nitrogen (the reader is referred to Chapter 8 for more information).

![Serration maps showing the temperature/strain rate conditions for different types of deformation behaviors observed in the (a) X52 and (b) X70 steels. Deformation behaviors (based on the classification system discussed in Table 4.1) are identified as uniform deformation (NO DSA), discontinuous propagation (DP), continuous propagation (CP), systematic nucleation (SN), and constrained nucleation (CN). Regions identified as high εc means the critical strain for serrations was relatively high and uniform deformation was observed prior to serrations and localized deformation. Open and filled shapes indicate regions of propagation and nucleation dominated deformation behaviors respectively. The dashed line in (a) indicates the maximum temperature where YPE and Luders bands were detected.](image)

The X52 and X70 steels exhibited several different deformation behaviors at different temperature-strain rate conditions within the DSA regime. The X52 and X70 steels exhibited distinct changes in deformation band behavior that were defined by linear lines on the serration maps. The lines that indicate changes in deformation behaviors are approximate boundaries based on the experiments performed. Note that the lower temperature boundary of the DSA regime for the X52 is approximated.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Strain Rate (s⁻¹)</th>
<th>Deformation Classification</th>
<th>Temperature (°C)</th>
<th>Strain Rate (s⁻¹)</th>
<th>Deformation Classification</th>
</tr>
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<tr>
<td>95</td>
<td>1.67 x 10⁻⁴</td>
<td>DP → CP</td>
<td>111</td>
<td>1.67 x 10⁻⁴</td>
<td>High εₛ CP</td>
</tr>
<tr>
<td>105</td>
<td>4.17 x 10⁻⁴</td>
<td>DP → CP</td>
<td>118</td>
<td>1.67 x 10⁻³</td>
<td>NO DSA</td>
</tr>
<tr>
<td>106</td>
<td>8.33 x 10⁻⁴</td>
<td>High εₛ CP</td>
<td>118</td>
<td>4.17 x 10⁻³</td>
<td>High εₛ CP</td>
</tr>
<tr>
<td>107</td>
<td>1.67 x 10⁻³</td>
<td>NO DSA</td>
<td>121</td>
<td>8.33 x 10⁻⁴</td>
<td>High εₛ CP</td>
</tr>
<tr>
<td>111</td>
<td>1.67 x 10⁻³</td>
<td>DP → CP</td>
<td>124</td>
<td>1.67 x 10⁻³</td>
<td>DP → CP</td>
</tr>
<tr>
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<td>8.33 x 10⁻⁴</td>
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<td>128</td>
<td>1.67 x 10⁻³</td>
<td>DP → CP</td>
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<tr>
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<tr>
<td>121</td>
<td>1.67 x 10⁻³</td>
<td>DP → CP</td>
<td>161</td>
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<td>DP → CP</td>
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<tr>
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<td>8.33 x 10⁻⁴</td>
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<tr>
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<td>1.67 x 10⁻⁴</td>
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<td>1.67 x 10⁻⁴</td>
<td>CN-CP</td>
</tr>
<tr>
<td>165</td>
<td>8.33 x 10⁻⁴</td>
<td>SN → CN-CP</td>
<td>165</td>
<td>1.67 x 10⁻³</td>
<td>DP → CP</td>
</tr>
<tr>
<td>166</td>
<td>1.67 x 10⁻³</td>
<td>SN → CN-CP</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Both steels exhibited relatively high critical strain (εᵥ) CP behavior (for an example refer to the X70 225 °C 10⁻⁴ s⁻¹ sample in Figure 4.5b) near the upper and lower boundaries of the DSA regime. Recall that critical strains were the amount of plastic deformation required for the onset of serrated yielding, which were discussed in the present work on a relative basis when comparing samples tested at the same strain rate (since engineering stress-time curves were used for the analysis). The high critical strain CP regions were observed over a narrow temperature range at all strain rates. At relatively low temperatures within the DSA regime, both steels exhibited propagating type deformation bands, mostly DP type at low strains that transitioned to CP at high strains. One testing condition of the X70 steel exhibited CP behavior throughout the tensile test (X70 149 °C 10⁻⁴ s⁻¹ in Figure 4.5a). The individual X70 CP sample was grouped with the DP → CP (DP at low strains with a transition to CP at high strains prior to plastic instability) samples, due to the primary mechanism of propagating deformation bands.

Deformation band nucleation behavior was observed at relatively high temperatures within the DSA regime for both steels. However, the serration morphologies and deformation band behaviors were slightly different for the two steels. In the X70 steel, deformation behavior transitioned from DP → CP (and CP in some cases) to CN-CP behaviors over a relatively narrow temperature range and then to SN → CP behavior. The X52 steel exhibited a transition from DP → CP to primarily SN → CN-CP behavior (a few samples exhibited CN-DP behavior at higher temperatures and strain rates). Prior to the high critical strain CP behavior near the high temperature boundary of the DSA regime, three samples in the X52 steel exhibited high critical strain CN-DP behavior (the X52 252 °C 10⁻³ s⁻¹ sample from Figure 4.9b and the stress-strain curves of the other two samples were reported in the MS thesis). The disappearance of Luders bands at the onset of yielding was also observed in the CN-DP region (indicated by the dashed line in Figure 4.15).
It was hypothesized that the changing serration morphologies and deformation behaviors at different temperature-strain rate conditions were due to changing mechanisms of the DSA phenomena. Two different solute-dislocation interaction models are primarily discussed in the DSA literature [13–25, 28–41]: the rapid pinning and unpinning of dislocations during deformation, and the permanent pinning of dislocations by solutes causing the rapid generation of new mobile dislocations to become necessary for deformation to continue. The latter model was typically associated with steels after Leslie’s [13, 14, 16] work, which showed a substantial increase in dislocation densities during DSA compared to room temperature results. It was speculated that changes in deformation behavior were a result of changing dislocation-solute interactions. More analysis and modeling of DSA mechanisms to predict deformation behavior is proposed in future work. More work regarding understanding local deformation behaviors associated with DSA over a wider strain rate range than $10^{-3}$ to $10^{-4}$ s$^{-1}$ is also proposed since a relatively small strain rate range was investigated in the present study.

### 1.23 Correlations Between Necking Morphologies and Strain Rate Sensitivities

Necking behaviors (briefly discussed in previous sections) were observed to change slightly for samples that exhibited uniform deformation or DSA. Figure 4.2b, 4.3a, 4.3b, and 4.3d showed that plastic instability (i.e. necking) in samples that exhibited uniform deformation (at temperatures above and below the DSA regime) initiated as diffuse necks, affecting almost the entire gauge length of the tensile sample. Incremental strain from necking then steadily concentrated to a smaller percentage of the gauge length (i.e. the width of the incremental strain peaks decreased) and the maximum incremental strain increased. Necking in samples that exhibited serrated flow shown in Figure 4.4-4.11 initiated from either CP or DP type deformation bands and the necks were typically more concentrated at the onset of plastic instability compared to samples that exhibited uniform deformation. However, all necking in X52 and X70 tensile samples was still classified as diffuse necks, which were primarily influenced by the round sample geometry. Also note that the flow curve morphologies for all pipeline steels tested in the MS and PhD work were classified as smooth and non-serrated (i.e. serrations from DSA were not observed past the point of instability).

The differences in the necking behaviors were hypothesized to be related to the negative strain rate sensitivities associated with DSA. Figure 4.16 shows a summary of the jump test strain rate sensitivity m-value measurements presented in Section 1.1. Strain rate sensitivities were negative when at least one strain rate condition of the jump test was within the DSA regime and positive when both strain rates exhibited uniform deformation. Recall that positive strain rate sensitivities indicate that the flow stress increases with an increase in the strain rate and vice-versa for negative strain rate sensitivities.
Figure 4.16 Summary figure of jump test strain rate sensitivity m-values measured at approximately 0.05 true strain for X52 and X70 steels. The shaded region defines the average DSA regime based on the observation of serrations in the jump test flow curves and the serration maps presented in Chapter 1.

Figure 4.17 shows example engineering stress-time curves, maximum local strain rates, and the corresponding incremental strain contour plots focusing on the transition from stable plastic flow (i.e. uniform deformation or deformation band propagation) to necking. The measured (maximum) strain rate in the X70 250 °C $10^{-4}$ s$^{-1}$ sample (Figure 4.17a) was approximately equal to the calculated engineering strain rate during uniform deformation. Upon the initiation of plastic instability, the maximum local strain rate (located at the center of the neck) increased linearly with a slope of approximately $1.5 \times 10^{-6}$ s$^{-2}$. The X70 250 °C $10^{-4}$ s$^{-1}$ contour plot showed that the incremental strain peak width of the neck decreased with increasing time/strain (i.e. the neck became more concentrated throughout the tensile test). The measured maximum local strain rate prior to necking in the X52 151 °C $10^{-4}$ s$^{-1}$ sample (Figure 4.17b) was slightly greater than the calculated engineering strain rate due to deformation band propagation from DSA (discussed above). Upon the initiation of plastic instability, the maximum local strain rate increased linearly with a slope of approximately $1.6 \times 10^{-6}$ s$^{-2}$, which was slightly greater than the slope of the sample that exhibited uniform plastic deformation in Figure 4.17a (which was tested at the same strain rate). As discussed above, the initiated neck in Figure 4.17a (with positive strain rate sensitivity) nearly affected the entire gauge length of the tensile sample, and the initiated neck in Figure 4.17b (with negative strain rate sensitivity) was more concentrated after nucleating from previous deformation bands.

Localized deformation (from deformation bands or necking) resulted in greater strain rate values compared to the engineering strain rate calculated for the tensile test because the “effective” gauge length (i.e. the gauge length of material deforming) was a fraction of the geometrical gauge length of the tensile sample. Theoretically, since the strain rate of the deforming material increased during plastic instability, the local flow strength within the neck changed relative to the sign of the strain rate sensitivity. Materials
with positive strain rate sensitivities would theoretically have a more diffuse neck geometry since the increased strain rate from the neck locally strengthens the sample. The local material away from the center of the neck (and the highest local strain rates) would be more favorable to deform due to the lower local flow strengths. However, the amount of deformation away from the center of the neck is also dependent on the local cross-sectional area of the sample. Negative strain rate sensitivities would theoretically result in a more concentrated neck because of the decreased local flow strength within the neck, which also has the smallest cross-sectional area of the sample. Thus, the center of the neck is the weakest point on a sample with negative strain rate sensitivity and concentrates the plastic deformation.

Figure 4.17 Engineering stress-time and associated contour plots of the incremental strain profiles of (a) X70 250 °C $10^{-4}$ s$^{-1}$ and (b) X52 151 °C $10^{-4}$ s$^{-1}$. Measured maximum local strain rate was overlaid on the engineering stress-time curves and the dashed line indicates the engineering strain for reference. Plot legends indicate the time increment used for the local strain rate analysis. (Color image, the reader is referred to the .pdf version of this document)

While the pipeline steels were strain rate sensitive, jump test m-values measured in the temperature range of 25-350 °C were typically less than 0.01, which translates to a change in flow strength of approximately 3-6 MPa between the $10^{-4}$ and $10^{-3}$ s$^{-1}$ strain rates. Such small changes in the flow strength were hypothesized to have only slight influences on the necking behavior. The tensile specimens that were influenced by DSA exhibited slightly more concentrated necking behaviors.
compared to the samples that exhibited uniform deformation, which supported the hypothesized influences of strain rates sensitivities on plastic instability discussed above.

1.24 Summary of Digital Image Correlation Testing

Recall that the first objective of the PhD work was to correlate physical deformation behavior to the flow curve morphologies of steels in the DSA regime. The purpose of the DIC study was to develop a greater fundamental understanding of the influences of DSA on the deformation behavior of pipeline steels at elevated temperatures. It was concluded that there was a strong correlation between flow curve morphologies and localized deformation behavior in the pipeline steels. The results presented in this chapter confirmed that localized deformation in materials influenced by DSA through interstitial-dislocation interactions can be systematically analyzed with DIC.

Five general types of deformation were observed in the X52 and X70 pipeline steels: uniform deformation, YPE/Luders band propagation, deformation band propagation, deformation band nucleation, and necking. Incremental strain analysis with DIC was used to correlate observed deformation behaviors to flow curve morphologies. Smooth flow curves were related to uniform deformation along the gauge length. Uniform deformation was observed at low temperatures (e.g. room temperature) and high temperatures (greater than 225-250 °C depending on the strain rate). Luders band propagation was observed at the onset of yielding for temperatures less than approximately 200-225 °C (depending on the strain rate) and was a result of static strain aging in the X52 steel. Deformation bands were a result of DSA. Deformation band propagation and nucleation were observed as continuous diagonal lines of intensity and discontinuities in the diagonal lines on the DIC contour plots respectively. Necking was identified as horizontal lines on the DIC contour plots.

Several different types of deformation band behaviors were identified in the pipeline steels and a new classification system for deformation behavior was proposed. Flow curve serration morphologies were divided into high and low frequency serration types. Low and high frequency serrations were associated with deformation band propagation and nucleation respectively. Two types of deformation band propagation and one type of deformation band nucleation were classified as primary deformation behaviors. Discontinuous propagation indicated unidirectional propagation of deformation bands with nucleation events at the ends of the gauge length, continuous propagation indicated the propagation of deformation bands up and down the gauge length, and systematic nucleation indicated quasi-random nucleation of deformation bands along the gauge length. Propagating type deformation behaviors were also observed with secondary (i.e. high frequency or Type B) serrations, which changed the deformation behavior from the propagation to nucleation of deformation bands. However, the overall deformation behavior was constrained to follow primary deformation characteristics.
Luders bands were associated with the greatest maximum local strain rates measured compared to deformation bands from DSA and early stages of necking. Maximum local strain rates associated with deformation band nucleation events were typically greater than measured values during deformation band propagation.

Steels typically exhibited high critical strain continuous propagation at high and low temperatures very close to the upper and lower boundaries of the DSA regime. Within the DSA regime, the steels typically exhibited deformation band propagation at relatively low temperatures and deformation band nucleation at relatively high temperatures.

Negative strain rate sensitivities associated with samples tested within the DSA regime influenced necking behaviors in the pipeline steel tensile samples. Samples that exhibited negative jump test strain rate sensitivity m-values had slightly more concentrated neck morphologies compared to samples with positive strain rate sensitivities. Necking initiated from previous CP or DP type deformation bands within the DSA regime and concentrated at a slightly higher rate than samples that exhibited uniform plastic deformation.
CHAPTER 5

THE EFFECT OF TEMPERATURE AND STRAIN ON ACTIVATION VOLUME AND INTERNAL/EFFECTIVE STRESS MEASURED WITH STRESS RELAXATION

Stress relaxation testing was performed to study changes in activation volumes and internal/effective stresses as a function of temperature and strain. As discussed in Section 3.6, two stress relaxation models were used independently to measure activation volumes and internal/effective stresses. This chapter includes results and discussion from stress relaxation measurements.

Stress relaxation tests were performed in the temperature range of 25-350 °C. Recall from Section 3.6, that testing conditions with highly localized plastic deformation (i.e. YPE with Luders bands or deformation bands with DSA) were considered invalid because of the possibility of non-uniform levels of relaxation along the gauge length of the specimens. Therefore, stress relaxation results discussed in this chapter only include testing conditions where uniform deformation was observed in the flow curve. Appendix D includes tables of all the stress relaxation parameters measured (including conditions that exhibited YPE or DSA).

1.25 Activation Volume Measurements

As introduced in Section 2.6.1, activation volumes were a measure of the volume of material swept through by mobile dislocations during a stress relaxation test, and the results are used to discern information about deformation mechanisms [84, 85, 132, 133]. The stress relaxation data were fit with Equation 2.4 using non-linear least squares regression for apparent activation volume measurements. Figure 5.1 shows the apparent activation volumes measured at various temperatures for the X52 and X70 steels as a function of engineering strain. All testing conditions exhibited apparent activation volumes below 100b³, which indicated that kink-pair migration dominated the deformation behavior of the pipeline steels (refer to Table 2.1). Samples also exhibited decay in the apparent activation volumes as a function of engineering strain. All X52 and high temperature X70 data (i.e. the 297 and 339 °C samples) superimposed over each other and exhibited approximately the same apparent activation volume values at all strains. The X70 25 and 246 °C samples exhibited slightly lower apparent activation volumes compared to the other X52 and X70 samples at low strains. However, all samples converged to approximately 7-10b³ at higher strains (further discussion of data is included below).

Kink-pair migration (or double kink segments) of screw dislocations to overcome the Peierls barrier is a well-established theory of plasticity for bcc metals [91, 132, 133]. Peierls barriers of $\frac{a}{2} \langle 111 \rangle$ screw dislocations in bcc engineering materials are typically exceptionally high due to the three-fold symmetry of the $\langle 111 \rangle$ axes [133]. Kink-pair migration is one method of allowing for dislocation
movement, without the need for the entire dislocation line to rigidly overcome the Peierls stress. Figure 5.2 shows a schematic representation of a dislocation in a bcc lattice using kink-pair migration to overcome the Peierls barrier. The activation volumes are given by: $V^* = bdL$, where $b$ is the Burgers vector, $d$ is the obstacle size (approximately equal to the distance between Peierls barriers, $\lambda$), and $L$ is the distance between obstacles (or opposite sign kinks). For bcc iron with a Burgers vector of 0.248 nm (1b), Argon [91] approximated the distance between Peierls barriers ($\lambda$) to be approximately 0.4 nm (1.6b), and Hull and Bacon [134] approximated the distance between segments to avoid attraction of opposite sign kinks (resulting in annihilation) to be on the order of 20b, resulting in a theoretical activation volume of $(1b)(1.6b)(20b) = 32b^3$. Lee et al. [84] approximated the distance between the Peierls barriers to be 1b, which would result in a theoretical activation volume of $20b^3$ for kink-pair migration. Lee et al. [84] and Gibbs [85] also discussed that the activation volume in bcc metals that have strong solute-dislocation interactions are on the order of $100b^3$. The apparent activation volumes measured for the pipeline steels were on the same order of the theoretical activation volumes (calculated above) for kink-pair migration in bcc crystals, and it was concluded that the kink-pair mechanism influenced by solute atoms likely dominated stress relaxation responses for all tests.

![Figure 5.1](image.png)

**Figure 5.1** Apparent activation volume as a function of engineering strain for the (a) X52 and (b) X70 steels tested at temperatures listed in the figure. For reference, room temperature conditions for both materials are included in each plot.

The decrease in apparent activation volume with strain observed in Figure 5.1 was hypothesized to be related to the effect of stress on the configuration of the kink-pair formation, modeled by Argon [91]. Argon’s analysis indicates that two regimes govern dislocation advance by repeated double-kink
nucleation. In Regime I, under low stress and/or at higher temperatures, the activation configuration of the kink pair consists of two weakly interacting fully formed kinks of opposite sign (note that kink segments are edge dislocations), where the applied stress holds the two apart. If the applied stress is too low and the distance between kinks is too small, the opposite sign edge segments attract and annihilate. With increasing stress, the equilibrium distance between kinks without annihilation (L) in the configuration decreases until the ends of the kinks touch.

The length of the kinks (d) in Regime I is approximately equal to the distance between the Peierls barriers (λ) (i.e. \( d \approx \lambda \)). In Regime II, which occurs at relatively higher stresses than Regime I, the length of the kinks in the configuration becomes progressively smaller with increased applied stress and the kink-pair no longer rests at the bottom of the Peierls barrier (i.e. \( d < \lambda \)). Therefore, in both regimes the activation volume decreases with increasing applied stress (due to decreased L in Regime I and decreased d and L in Regime II). The following equations are the models derived by Argon [91] for Regimes I and II respectively

\[
\Delta v_{\alpha I}^* = \frac{1}{\pi^2} \left( \frac{1 + \nu}{1 - \nu} \right) \left( \frac{\mu}{\bar{\varepsilon}_s^2} \right)^{1/2} \left( b \lambda \right)^{3/2} \left( \frac{\bar{\varepsilon}_s}{\sigma_s} \right)^{1/2} \\
\Delta v_{\alpha II}^* = \frac{\pi}{2} \left( \frac{\mu}{\bar{\varepsilon}_s^2} \right)^{1/2} \left( b \lambda \right)^{3/2} \left( 1 - \frac{\sigma_s}{\bar{\varepsilon}_s} \right)
\]
where $\Delta v^*_i$ is the activation volume in Region $i$, $v$ is Poisson’s ratio, $\mu$ is the shear modulus, $\tau_x$ is the athermal component of the shear flow stress (i.e. internal stress) at $T = 0$ K, and $\sigma_x$ is the applied stress.

Figure 5.3a shows a schematic of kink-pair configurations under an applied stress for Argon’s [91] kink-pair models (Regimes I and II introduced above). Figure 5.3b shows activation volume as a function of applied stress for Regimes I and II, outlined in Equations 5.1 and 5.2 and overlaid on experimental data from single crystal high purity Mo, tested by Hollang et al. [133]. Activation volumes of the Mo single crystals were measured using stress relaxation methods (whose experimental procedure was nearly identical to the experiments in the present document). Note that Hollang et al. [133] performed stress relaxation measurements at various temperatures; however, Argon [91] did not report the temperature for the data generated in his model. Upon further inspection of the stress-strain curves reported by Hollang et al. [133], it was interpreted that the testing temperature of the data shown in Figure 5.3b was the 218 K (-55 °C) testing condition. Strain hardening enabled activation volumes to be measured at increasing applied stress levels using stress relaxation measurements. Activation volumes in Regime I decreased with the approximate shape of a parabolic function as the length $L$ of the kink-pairs decreased with increasing applied stress. Activation volumes in Regime II decreased linearly with increasing applied stress. The functionality of the activation volume measurements in the pipeline steels exhibited approximately the same behavior as the Regime I (low stresses and/or high temperatures) kink-pair model predicted. Activation volumes reported by Hollang et al. [133] in the Mo crystal were in the range of $10^{-30}b^3$ and the activation volumes measured in the pipeline steels were in the range of approximately $8-82b^3$. The relatively large activation volumes measured in the pipeline steels (observed in measurements at relatively low strains in Figure 5.1) compared to the Mo single crystals from Hollang et al. [133] were hypothesized to be a result of solute atoms in the steel microstructures, as Gibbs [85] and Lee et al. [84] indicate that solute atoms in bcc structures typically results in activation volumes on the order of $100b^3$, compared to the $10-100b^3$ activation volumes reported for kink-pair migration.

At room temperature and relatively low strains, activation volumes measured in the X52 steel were slightly greater than that of the X70 steel (e.g. in Figure 5.1a at approximately 2.7 pct strain, the apparent activations volumes for X52 and X70 steels were approximately $59b^3$ and $42b^3$ respectively). It was hypothesized that differences in chemical composition regarding elements that can influence solid solution strengthening/softening (C, Mn, Si, Ni, Cr, Mo, etc.) and/or differences in interstitial atom concentrations could account for the activation volume differences between the two steels. For example, internal friction data (discussed in Chapter 8) indicated that the X70 steel had a lower interstitial carbon concentration than the X52 steel. The lower concentration of interstitial carbon could explain the slightly lower activation volumes measured in the 25 °C X70 sample. At high strains, apparent activation volumes were approximately the same for all X52 and X70 samples (further discussion included below).
Figure 5.3 (a) Schematics of kink-pair configuration models under applied stresses in Regimes I and II. At low stresses and high temperatures (Regime I) the kinks are well separated and fully formed, at high stresses the geometry is more of a bulge, where only a portion of the dislocation line is over the peak of the Peierls energy ridge. (b) The effect of applied stress on the activation volume modeled and experimentally obtained for single crystal high purity Mo. Figures adapted from Argon [91] where experimental data were provided by Hollang et al. [133].

Activation volumes measured in the X52 steel (Figure 5.1a) were approximately the same for all temperatures at equivalent strains. The higher temperature X70 samples (X70 297 and 339 °C) also exhibited approximately equivalent activation volumes compared to the X52 steel samples. However, the activation volumes measured in the X70 steel (Figure 5.1b) were 10-20\% larger for the 297 and 339 °C conditions at low strains compared to the lower temperature experiments.

The activation volume data from Figure 5.1 were plotted as a function of the flow stress (measured at the start of each relaxation) to compare the pipeline steel behavior to the models outlined by Argon [91] in Equations 5.1 and 5.2. Different stress levels were achieved in the pipeline steel samples, due to strain hardening from relaxations measured at different strains throughout the tensile test. Figure 5.4 shows the apparent activation volume measurements as a function of the true flow stress at the start of the stress relaxation test for the X52 and X70 steels. The data depicted in Figure 5.4 approximately followed the same behaviors that were discussed with respect to Figure 5.1. Only slight differences in activation volumes were detected for the X52 steels at all flow stresses and the high temperature.
conditions (greater than approximately 300 °C) of the X70 steels exhibited higher activation volumes compared to low temperature samples at equivalent stress levels. Data from complementary testing techniques are needed for further discussion of differences in activation volume behaviors in the pipeline steels. The reader is referred to Chapter 9 for further discussion.

Figure 5.4 Apparent activation volumes as a function of flow stress for the X52 and X70 samples. Flow stresses were measured at the start of the stress relaxation tests (i.e. t = 0 s). The activation volume values presented are equivalent to data shown in Figure 5.1, except that flow stress values were measured at the engineering strains reported at the start of the stress relaxation tests.

1.26 Internal/Effective Stress Measurements

Internal and effective stresses were deconvoluted from flow stresses using the procedures outlined in Section 3.6.2. Recall that internal and effective stresses are related to long range (e.g. dislocation interactions, precipitates and grain boundaries) and short range (e.g. Peierls stress and solute-dislocation interactions) stress fields, respectively. From first principles, the effective stress is strongly dependent on strain rate, and temperature and the internal stress is strongly dependent on the plastic strain [81–83]. Measurements of internal/effective stresses were used to make inferences on influences of strengthening mechanisms on the flow stresses of the pipeline steels at different testing temperatures.

Figure 5.5 and 5.6 show measured flow, internal, and effective stresses at various temperatures as a function of engineering strain in the X52 and X70 steels respectively. The X52 25 °C and 245 °C samples (Figure 5.5a and 5.5b) exhibited YPE and the 245 °C sample exhibited high critical strain
continuous propagation (CP) type serrations/deformation bands from DSA (regions are indicated in the figures). As discussed above, stress relaxations in the presence of Luders/deformation bands were considered invalid for stress relaxation analysis.

Figure 5.5 Internal and effective stresses compared to flow stress in X52 samples tested at (a) 25 °C, (b) 245 °C, (c) 295 °C, and (d) 338 °C. Error bars represent the range of internal/effective stress values calculated for $n \approx \theta_0$ stress combinations in each relaxation curve. Flow stresses were measured at the start of the stress relaxation test (i.e. $t = 0$ s).

Effective stress was approximately constant as a function of engineering strain at strains greater than approximately 3 pct for all samples. Internal stress also increased as a function of strain for almost all testing conditions. However, some samples exhibited behaviors that differed from what was expected based on first principles assumptions. At room temperature for both materials (Figure 5.5a and 5.6a), the effective stress values were 100-150 MPa higher at low strains (just past the YPE region for X52) compared to the high strain conditions. It was hypothesized that at low strains, the flow stresses of the
materials were affected by static strain aging, which resulted in increased effective stress levels and at high strains the effective stress was primarily influenced by the Peierls stress and the Snoek effect during dislocation movement (as discussed by Schoeck and Seeger [81] and depicted in Figure 2.14a). However, the hypothesized effective stress response of static strain aging at low strains fails to explain the corresponding relatively low internal stress values observed at low strains in the 25 °C samples compared to higher temperature conditions. High temperature conditions also tended to exhibit slightly lower effective stress measurements at low strains. However, changes in effective stress were typically small (less than 60 MPa) and might be a result of measurement errors between relaxations.

![Figure 5.6 Internal and effective stresses compared to flow stress in X70 samples tested at (a) 25 °C, (b) 246 °C, (c) 297 °C, and (d) 339 °C. Error bars represent the range of internal/effective stress values calculated for n ≈ 60 stress combinations in each relaxation curve. Flow stresses were measured at the start of the stress relaxation test (i.e. t = 0 s).](chart.png)
The X52 245 °C sample (Figure 5.5b) was somewhat unique, due to the testing conditions proximity to the upper bound of the DSA regime (see Figure 4.15 for reference), resulting in high critical strain CP serrations and uniform deformation at low strains. As the material approached the critical strain for serrated yielding (and DSA conditions), the effective stress increased by approximately 100 MPa. The increase in effective stress near the critical strain indicated that solute-dislocation interactions influenced the flow stress more strongly near DSA conditions.

Internal and effective stresses were normalized by the flow stress to make direct comparisons between samples, since relatively large strength changes were observed at different testing temperatures. Normalized internal and effective stresses essentially indicated the percentage of the flow stress influenced by long range and short-range stress fields respectively. Figure 5.7 shows internal and effective stress measurements normalized by the flow stress for the X52 and X70 samples. Normalized internal and effective stresses were approximately constant as a function of strain for all samples, except for the room temperature samples hypothesized to be influenced by static strain aging at low strains, and the X52 245 °C sample near DSA conditions that exhibited greater effective stresses compared to the room and high temperature samples. Discussions of the room temperature samples below refer to values measured at relatively high strain conditions (greater than approximately 3 pct) that are comparable to the values measured in the higher temperature experiments. The X52 conditions outside the DSA regime exhibited approximately strain-independent internal and effective stresses as a function of temperature, which indicated that tests were performed in regions A and B relative to Figure 2.14a.

Figure 5.7 Internal and effective stresses normalized by the flow stress as a function of engineering strain for the (a) X52 and (b) X70 steels.
Similar to the X52 samples, the X70 25 and 245 °C testing conditions exhibited approximately equivalent internal and effective stresses. However, the X70 295 and 338 °C samples exhibited relatively higher normalized internal stress values (and subsequently lower effective stress values) compared to the lower temperature conditions. Increased internal stress values indicated that strengthening mechanisms from long-range stress fields had a greater influence on the flow stress at high temperatures compared to low temperatures in the X70 steel. Reduced relative effective stresses were hypothesized to be caused by the inverse relationship between effective stress and temperature (refer to Figure 2.14 and Section 2.6). Hypothesized causes of the increased internal stress values were the dynamic precipitation of carbides during deformation or increased strain hardening from relatively higher dislocation densities in the high temperature samples. Such hypotheses were tested with complementary characterization techniques discussed in the subsequent chapters. More discussion of the stress relaxation measurements compared to x-ray diffraction, microscopy, and internal friction testing techniques are included in Chapter 9.

1.27 Summary of Stress Relaxation Results

Stress relaxation experiments were used to assess activation volumes and internal/effective stresses in pipeline steels. Activation volume measurements less than 100b\(^3\) were observed in the pipeline steels at all testing conditions, indicating that kink-pair migration of screw dislocations in the ferrite dominated stress relaxation responses in the steel samples. Activation volumes related to kink pair migration are dependent on the distance between kinks, the length of the kinks, the Burgers vector, and the presence of solute atoms for solid solution strengthening (which increases activation volume). Activation volumes for the X52 steels were approximately the same for all testing conditions. However, the X70 samples tested at high temperatures exhibited greater activation volumes at low strains compared to the low temperature conditions.

Samples tested at conditions near static (low strains at relatively low temperatures in both X52 and X70) or dynamic strain aging conditions exhibited greater effective stresses compared to samples tested outside the DSA regime. It was hypothesized that the strong solute-dislocation interactions near conditions exhibiting YPE and strain aging were responsible for the increased effective stresses observed. All X52 samples tested at strains greater than approximately 3 pct exhibited approximately the same normalized internal and effective stresses. In contrast, the high temperature conditions of the X70 samples exhibited increased normalized internal stresses and decreased effective stresses. Increased internal stresses were hypothesized to be a result of dynamic precipitation or increased dislocation densities relative to the lower temperature samples. Complementary testing techniques were required for further discussion of the stress relaxation results.
CHAPTER 6

X-RAY DIFFRACTION PHASE AND DISLOCATION DENSITY ANALYSIS

X-ray diffraction (XRD) and wide-angle x-ray scattering (WAXS) were used to characterize phase and dislocation density changes (as a semi-quantitative analysis) in the pipeline steels after straining at various temperatures. Preliminary XRD experiments were performed at the laboratory scale but the primary focus of diffraction analysis was with synchrotron data. Since multiple x-ray energies were used for diffraction analysis, plots in this chapter are of normalized intensity as a function of d-spacing (on a descending scale so the data are oriented the same as two-theta plots) for easy comparison between results.

1.28 Phase Analysis with Laboratory X-Ray Diffraction

Laboratory XRD was used to gain a preliminary understanding of the phases present in the X52 and X70 steels. Figure 6.1a and 6.1b present XRD line scans of the as-received X52 and X70 steels measured with the longitudinal direction normal to the plane of the polished sample. A Cr source was used to obtain the greatest signal to noise ratio possible with the CSM diffractometer. Both materials exhibited ferrite ($\alpha$) (110), (200), and (211) peaks located at approximately the same d-spacing values relative to each other as the highest intensity peaks detected. The X52 and X70 steels have mostly ferritic microstructures (refer to Figure 3.1), and it was anticipated that the ferrite peaks would have the greatest intensity in XRD. Figure 6.1c and 6.1d show higher magnifications of the diffraction line scans of the X52 and X70 steels respectively. Two low intensity peaks in the X52 steel were located at approximately 2.01 and 2.00 Å (slightly lower d-spacing values than the $\alpha$ (110) peak) and were hypothesized to be cementite ($\text{Fe}_3\text{C}$) (031) and (112) diffraction peaks, based on simulations with HEXRD (2.01 and 1.98 Å respectively) and observed pearlite ($\alpha$+Fe$_3$C microconstituent) in the microstructure shown in Figure 3.1. Low intensity austenite ($\gamma$) (111) and (200) peaks were detected in the X70 steel (Figure 6.1d). Peak d-spacing values for the detected austenite peaks closely matched the simulated peaks form HEXRD. Since the austenite peaks were low intensity and the X70 steel is heavily textured, accurate volume fraction measurements were unreliable. However, volume fractions of the secondary phases were estimated to be less than 2 pct based on detection limits of the CSM diffractometer. Fe$_3$C was potentially detected in the as-received X70 steel. Figure 6.1e shows the as-received X52 and X70 line scans superimposed over each other. A protrusion from the X70 $\alpha$(110) was observed at the location of the hypothesized $\text{Fe}_3\text{C}(031)$ peak observed in the X52 sample. The peaks in the X70 steel were slightly broader compared to peaks in the X52 steel (likely due to higher dislocation density and smaller grain size of the X70 steel), which could have masked the presence of near-by low intensity secondary phase peaks.
Figure 6.1  X-ray diffraction line scans of the as-received (a) X52 and (b) X70 steels with the Cr-source with ferrite ($\alpha$) peaks indexed. Figures (c) and (d) are higher magnification images of the as-received X52 and X70 steels, respectively, showing the detected lower intensity peaks hypothesized to be austenite ($\gamma$) and Fe$_3$C. (e) X52 and X70 scans superimposed over each other, showing the possibility of Fe$_3$C in X70 (Color image, the reader is referred to the .pdf version of this document).
Laboratory XRD scans were also performed on coupons sectioned from the gauge sections of tensile bars tested at approximately 25 and 200 °C (strain levels are approximately equal to the uniform elongations reported in Figure 1.4 for the $10^{-4}$ s$^{-1}$ data). Figure 6.2 shows partial XRD scans of the X52 and X70 samples in the as-received and strained conditions superimposed over each other. Temperature and strains are indicated for each line scan (e.g. X52 25 °C 14.4 pct indicates a sample tested at room temperature and the uniform elongation was 14.4 pct). It was assumed that the different strain levels of each sample had negligible influence on the observations discussed in the present section.

![Figure 6.2](image)

Figure 6.2 X-ray diffraction line scans showing the effects of $\alpha(110)$ peak broadening after straining at room temperature and approximately 200 °C on the detection of low intensity peaks in (a) X52 and (b) X70 scans. Scans are indicated as as-received or by the deformation temperature and imposed strain of the samples (which was approximately equal to the uniform elongation). (Color image, the reader is referred to the .pdf version of this document)

Peak broadening of the $\alpha(110)$ peak was observed for both steels and the 200 °C conditions exhibited greater extents of line broadening compared to the 25 °C samples, which was likely due to higher dislocation densities generated within DSA conditions. The broadened $\alpha(110)$ peaks in the strained samples masked the appearance of the hypothesized Fe$_3$C peaks observed in the as-received conditions. The X70 steel also exhibited slight changes in the low intensity $\gamma(111)$ after straining at 25 and 200 °C. The change in magnitude of the $\gamma(111)$ was hypothesized to be a result of either stress/strain assisted transformation (i.e. the TRIP effect) or decomposition of the austenite. The austenite peaks observed in the laboratory XRD experiments were too low in magnitude for further analysis. As discussed below,
Synchrotron WAXS was performed to better characterize secondary phases present with quasi-polygonal ferrite.

1.29  **Synchrotron Wide-Angle X-Ray Scattering Analysis**

Synchrotron WAXS was used to study phases in the pipeline steels. Note that normalized peak intensities were tabulated and provided for reference in Appendix E. Ferrite and austenite (to a limited extent) phases were detected with laboratory XRD (discussed above). Synchrotron diffraction data allowed for higher sensitivity detections of low volume fraction phases in the pipeline steels (i.e. austenite and potentially carbide phases). Figure 6.3 shows diffraction line scans of the as-received X70 steel measured with laboratory XRD and synchrotron WAXS from CHESS and APS superimposed over each other. Normalized intensity was plotted on a logarithmic scale, so all the peaks could be observed. Ferrite peaks (and austenite observed with XRD) are identified on the figure. The three measurement methods exhibited excellent repeatability with respect to the locations of d-spacing values for the ferrite and austenite peaks compared to each other. The Cr-Source in the XRD results covered a smaller range of d-spacings compared to the WAXS results, which limited the number of ferrite peaks observed (i.e. 3 ferrite peaks were observed in XRD and 5 to 8 ferrite peaks were observed with WAXS). Synchrotron WAXS line scans also exhibited up to one order of magnitude lower background intensities compared to the XRD results. The low background intensities of WAXS enabled the detection of low intensity peaks of either primary phases at low d-spacing values, or small volume fraction phases at high d-spacing values. Data generated at APS exhibited the widest range of d-spacing values measured and appeared more sensitive with respect to detecting low intensity peaks compared to the CHESS results. It was hypothesized that the APS x-ray beam was more monochromatic compared to the CHESS x-ray beam, which allowed for higher sensitivities to detect low intensity peaks.

Synchrotron WAXS tested at CHESS was performed with different beam sizes and detector frame rate conditions to test the sensitivity of a new high frame rate detector being developed for the F2 beamline. Figure 6.4 shows the effect of detector frame rate and beam size on the WAXS line scans of the as-received X70 steel. Beam sizes of 100x100, 200x200, and 500x500 μm were tested at 10 and 100 Hz detector frame rates. Recall from Section 3.7.2 that the CHESS line scans are averaged intensities from all the frames in a 1.0 s scan. The 10 and 100 Hz conditions are therefore, averages of 10 and 100 different sets of diffraction data respectively. The relative location of the beam on the sample was constant for all CHESS measurements. Intensity minima located at approximately 1.6 and 1.1 Å in the CHESS diffraction patterns were a consequence of the spaces between the x-ray detectors (see Section 3.7.2) having zero measured intensity and phase analysis was limited in these regions. The diffraction pattern from APS (red line) is plotted in Figure 6.4 for reference as well.
Detector frame rate had little influence on the ferrite peaks and the data plotted in Figure 6.4 focused on detection of the low intensity peaks. Higher detector frequencies resulted in increased background noise levels for all beam size conditions. However, the 100x100 μm beam size (Figure 6.4a) exhibited the greatest background noise levels at 100 Hz compared to the larger x-ray beams (Figure 6.4b and c). The 10 Hz condition was therefore selected for further analysis.

Low intensity peaks were observed in the CHESS data at 2.08, 1.81, 1.28, 1.09, and 1.04 Å d-spacings for all beam size and detector frequency conditions. The relative peak heights of the low intensity peaks were approximately constant for the 200x200 and 500x500 μm beam sizes. However, the 10 Hz 100x100 μm condition exhibited slightly lower peak heights compared to the higher frequency condition. Although, the maximum differences were only approximately 0.002 normalized intensity different compared to each other. It was concluded that changing beam/detector conditions in the CHESS WAXS data only had slight influences on results. The 100x100 μm beam size was selected for further phase analysis to allow for constant beam geometry between the APS and CHESS measurements.
Figure 6.4 WAXS line scans from as-received X70 showing the effect of detector frame rate (10 and 100 Hz) on the background and low intensity peaks at different beam sizes of (a) 100 x 100 μm, (b) 200 x 200 μm, and (c) 500 x 500 μm from the CHESS results. Line scans from APS are plotted (red) for reference. (Color image, the reader is referred to the .pdf version of this document)
1.29.1 As-Received Pipeline Phases

As discussed above, several secondary phase peaks were observed in the synchrotron diffraction data. Figure 6.5 shows the WAXS diffraction patterns of as-received X70 (from APS and CHESS measurements) and X52 (from CHESS) samples. Austenite peaks were indexed for the X70 steel and selected peaks, hypothesized to be from cementite in the X52 steel are also indicated in Figure 6.5. The wide d-spacing range and high detector sensitivities enabled the observation of several austenite peaks in the X70 samples (including relatively high index peaks like the $\gamma(222)$ at 1.0 Å or the $\gamma(242)$ at 0.81 Å).

It was concluded that only ferrite and austenite peaks were distinctly visible in the X70 CHESS diffraction spectra, since all diffraction peaks were indexed using ferrite or austenite lattice parameters. The X52 steel exhibited protrusions in the $\alpha(110)$ peak at d-spacings of 2.13 and 2.09 Å, as well as a low intensity peak at 1.87 Å. The low intensity peaks in the X52 steel were hypothesized to be from cementite, based on microstructural observations of pearlite in Figure 3.1.

![Figure 6.5 WAXS line scans of as-received X52 and X70 steels with indexed ferrite and austenite peaks.](Color image, the reader is referred to the .pdf version of this document)
Several low intensity peaks were observed in the X70 APS diffraction data at relatively high d-spacings (i.e. near the \(a\langle 110\rangle\)) that were hypothesized to be caused by carbides and nitrides in the steels. Hypothesized carbides/nitrides included: cementite, transition carbides (epsilon, eta, and H\"ag\"g carbides), and microalloy carbides/nitrides (from niobium and titanium additions). Lattice parameters for the hypothesized carbides were shown in Table 3.4 and calculated d-spacings for theoretical diffraction peaks are included in Appendix A. Carbides and nitrides present in the quasi-polygonal ferrite microstructure were likely small (on the order of tens of nm) and present at low volume fractions (investigated with transmission and scanning electron microscopy in Chapter 7).

Figure 6.6 shows the as-received X70 diffraction data from APS with indexed ferrite and austenite peaks and locations of the theoretical carbide/nitride peaks (indicated by the data points and simulated with HEXRD®) potentially present in the quasi-polygonal ferritic microstructure. Due to the high number of potential phases (some of which had large numbers of diffraction peaks from orthorhombic or monoclinic crystal structures that have approximately the same d-spacings), it was challenging to fully index the low intensity peaks from the APS data. However, it was hypothesized that cementite and H\"ag\"g carbide peaks were observed in the as-received X70. A few theoretical cementite peaks (square data points in Figure 6.6) exhibited unique d-spacings between 1.88-1.85 \(\text{Å}\), where one distinct peak was observed in the diffraction data (at 1.88 \(\text{Å}\)), which supported the presence of cementite precipitates in the microstructure. Other potential cementite peaks were located at 2.54 and 1.96 \(\text{Å}\). Theoretical H\"ag\"g carbide peaks (diamond data points in Figure 6.6) also exhibited unique d-spacings compared to the other theorized carbide/nitride phases at 1.92 and 1.91 \(\text{Å}\), where one distinct peak was observed in the diffraction data (at 1.91 \(\text{Å}\)). Other potential H\"ag\"g carbide peaks observed were located at 2.49, 2.28, 2.20 \(\text{Å}\).

It was determined that epsilon carbide was undetected in the X70 steel, since only background intensity was observed near the theoretical peak locations. One low intensity carbide/nitride peak most closely matched eta carbide at 1.61 \(\text{Å}\) (circle data points in Figure 6.6). However, it was determined that the presence of eta carbide was unlikely, since only background intensity was observed at other theoretical peak locations (especially between 2.42 and 2.35 \(\text{Å}\)). A few of the low intensity diffraction peaks matched theoretical locations for the potential microalloy precipitates (e.g. NbN at 2.54 and 2.20 \(\text{Å}\) that overlapped with hypothesized cementite and H\"ag\"g carbide peaks respectively, and TiC at 2.49 \(\text{Å}\) that overlapped with a hypothesized H\"ag\"g carbide peak). However, results regarding microalloy precipitates were inconclusive due to the lack of distinct unique peaks.
Figure 6.6  WAXS line scan of as-received X70 from the APS results, showing low intensity peaks around the $\alpha$(110) peak. Ferrite and austenite peaks are identified. Data points indicate the theoretical locations of peaks from Fe$_3$C, transition carbides, and microalloy carbides/nitrides generated with HEXRD®.

1.29.2 Phase Changes During Elevated Temperature Deformation

Synchrotron WAXS testing was performed on tensile and internal friction specimens pre-strained at various temperatures. Figure 6.7 shows diffraction line scans of X70 samples strained at temperatures less than 300 °C (black and blue lines) compared to the as-received APS data (red lines). Samples strained to approximately 5 pct were measured at CHESS and higher strains were measured at APS. Samples strained at temperatures between 25 and 250 °C exhibited only subtle differences in low intensity diffraction peaks compared to the as-received material. The peak located at 2.20 Å disappeared after straining at all temperatures. However, all other peaks (including austenite peaks) were still observed after tensile deformation. With increasing straining temperature, the austenite peaks exhibited slight decreases in normalized intensity up to 250 °C.

Figure 6.8 shows diffraction line scans of X70 samples strained at 300 and 350 °C (black and blue lines) compared to the as-received APS data (red lines). In contrast to the lower temperature samples in Figure 6.7, the specimens tested at 300 and 350 °C exhibited noticeable differences in diffraction patterns compared to the as-received condition. Austenite peaks exhibited substantial decreases in diffracted intensity in the samples strained to approximately 5 pct (black lines), and austenite was undetected in samples strained to the uniform elongation (blue lines). Note that samples indicated with approximately 5 pct deformation were from interrupted tensile tests (where local strain at the approximate location of the x-ray beam was measured with DIC).
Figure 6.7  WAXS scans of X70 samples strained at approximately (a) 25 °C, (b) 200 °C, and (c) 250 °C compared to the as-received material. Samples with approximately 5 pct strain were measured at CHESS and samples with higher strains were measured at APS. The higher strains represent the uniform elongation of the X70 samples and lower strains were from interrupted tensile tests. (Color image, the reader is referred to the .pdf version of this document)
It was hypothesized that the decreases in austenite peak intensities were associated with decomposition of the retained austenite in the quasi-polygonal ferrite microstructure. Peaks hypothesized to be diffraction of carbide/nitride phases were also undetected after deformation at temperatures greater than or equal to 300 °C. One exception was the low intensity peak at 1.96 Å, potentially associated with cementite, eta, and Hägg carbide theoretical peak d-spacings (refer to Figure 6.6), that was visible in all strained conditions. The loss of nearly all the carbide peaks was hypothesized to be associated with the dissolution of transition carbides, which would indicate that the peak at 1.96 Å was a result of diffraction of cementite. Complementary characterization techniques were required for further discussion.

![Figure 6.8](image.png)

**Figure 6.8** WAXS scans of X70 samples strained at approximately (a) 300 °C and (b) 350 °C compared to the as-received material. Samples with approximately 5 pct strain were measured at CHESS and samples with higher strains were measured at APS. The higher strains represent the uniform strain of the X70 samples and lower strains were from interrupted tensile tests. *(Color image, the reader is referred to the .pdf version of this document)*
The strain dependence of austenite decomposition was investigated by comparing WAXS measurements in the grip and gauge sections of internal friction samples strained at 300 and 350 °C to approximately 5 pct. The grip section exhibited zero plastic strain and was exposed to the same temperature history as the strained gauge section. Figure 6.9 shows the WAXS measurements of 300 and 350 °C samples with zero and 5.1 pct strain from the CHESS study. Samples were at temperature for approximately 2100 s. At 300 °C, austenite decomposition was only noticeable in the strained condition. Strains greater than 5.1 pct were required for complete austenite decomposition, since the $\gamma$(111) and $\gamma$(200) peaks were still visible with decreased intensities. The 350 °C sample exhibited evidence of incomplete austenite decomposition in the zero-strain condition. Austenite peaks in the 350 °C 5.1 pct strain condition exhibited evidence of more complete decomposition of austenite compared to the zero-strain condition. The $\gamma$(111) was the only peak observed in the 350 °C 5.1 pct condition and the normalized intensity was approximately half of the zero-strain condition. It was concluded that austenite decomposition was accelerated during straining. However, given sufficient time, it was hypothesized that complete austenite decomposition was possible without strain at temperatures greater than 300 °C.

Figure 6.9 WAXS scans of X70 samples showing the effects of strain on austenite decomposition at temperatures greater than 300 °C. Black and blue curves represent diffraction data measured from the gauge and grip sections of a strained internal friction sample respectively. Samples were at temperature for about 2100 s. (Color image, the reader is referred to the .pdf version of this document)
1.30 Williamson-Hall Dislocation Density Analysis

The modified Williamson-Hall analysis was performed on the APS diffraction data to approximate changes in relative dislocation densities of the strained samples. Dislocation density analysis was also performed with data from the CHESS study and the results were inconclusive. The experimental x-ray detector that was being tested during the CHESS study was not optimized for peak broadening analysis [136]. Measurements on an area detector convolutes where x-rays are emitted from the sample and the angle at which they are emitted. The convolution gets worse as the sample thickness increases. More accurate measurements of peak width are possible with synchrotron XRD by using an analyzer crystal placed downstream from a diffracted beam. The analyzer crystal diffracts at a known angle into a point detector. Rocking the analyzer crystal over the diffracted beam allows for deconvolution of strain and grain size broadening from the position broadening of the beam [136]. The experiments performed at APS also used an area detector and were subject to the same uncertainties discussed above regarding the CHESS analysis. Decomposition of austenite and dissolution of carbide phases could have influenced ferrite peak broadening as well. Dislocation density data discussed in this section were considered as semi-quantitative observations used as complementary information to support analysis from other characterization techniques.

Figure 6.10 presents the results of the relative dislocation density measurements in tensile samples deformed at various temperatures. The numbers next to each data point indicated the measured uniform elongation of the tensile specimens (see Figure 1.4c). The room temperature sample with approximately 9.5 pct strain, exhibited the lowest relative dislocation density compared to the high temperature tests. The 202 and 230 °C samples with approximately 7 pct strain and tested within the DSA regime (refer to the serration map in Figure 4.15), exhibited lower uniform elongation and higher relative dislocation density values compared to the room temperature sample. Leslie [13] concluded that steels exhibited greater dislocation densities during DSA as a consequence of solutes pinning dislocations which required the generation of new dislocations for deformation to continue (refer to Figure 2.3). The observed dislocation density measurements in the X70 steel supported Leslie’s [13] findings. Samples tested at higher temperatures also exhibited increased relative dislocation densities compared to the room temperature sample and samples tested in the DSA regime. Relatively high dislocation densities in the high temperature samples were hypothesized to be related to the increased strength observed in the X70 steels outside the DSA regime. Further discussions regarding dislocation densities are included in Chapter 9.
Figure 6.10 Williamson-Hall dislocation density measurements as a function of testing temperature from the APS WAXS results. Strains (indicated above data points) varied between samples and were approximately equal to the uniform elongation (UE).

### 1.31 Summary of Diffraction Results

Ferrite and austenite phases were identified with laboratory and synchrotron diffraction techniques. Austenite volume fractions were hypothesized to be small (less than 2 pct) based on the low intensity peaks observed. Strain assisted austenite decomposition was observed in samples tested at 300 and 350 °C. Evidence of partial austenite decomposition in un-strained samples heated to 350 °C was observed. However, the extent of decomposition was greater in strained samples with equivalent heating histories. Peaks hypothesized to be diffraction of cementite and Hägg carbide were also observed in the synchrotron WAXS data for as-received and 25-250 °C strained samples. The low intensity carbide peaks disappeared in samples strained at 300 and 350 °C. One carbide peak, that was hypothesized to be diffraction of cementite, remained in the samples strained at 300 and 350 °C.

Relative dislocation density measurements were performed with the modified Williamson-Hall analysis on the APS synchrotron WAXS data. Samples that exhibited DSA resulted in greater relative dislocation densities compared to the sample strained at room temperature. However, the samples with the greatest relative dislocation densities were tested at temperatures greater than the upper boundary of the DSA regime.
Scanning and transmission electron microscopy (SEM and TEM) were used to observe microstructural features in the X70 steel after deformation at various temperatures. This chapter includes the results and discussions of the microscopy analysis. Figure 7.1 shows an SEM image of the as-received X70 steel introduced in Section 3.2. The microstructure was classified with a quasi-polygonal ferrite (“F” in images) morphology with single and two-phase microconstituents observed. The single and two-phase microconstituents were hypothesized to be austenite (“A”) and martensite-austenite (“MA”) islands respectively. Fine particles, randomly dispersed in the quasi-polygonal ferrite grains were hypothesized to be carbides (identified by “C” with arrows in images). Carbide sizes observed in SEM images were on the order of 30-100 nm in diameter. Austenite and MA islands were typically on the order of 1-2 μm.

Figure 7.1 (a) Scanning electron micrograph showing the characteristic microstructure of as-received X70. Quasi-polygonal ferrite (F) and microconstituents hypothesized to be austenite (A) and martensite-austenite (MA) islands are indicated and higher magnifications of the microconstituents are shown in (b) and (c). Fine particles randomly dispersed in ferrite grains were hypothesized to be carbides (C). Images are oriented with the plate longitudinal and normal directions oriented horizontally and vertically respectively. Sample etched with 2 pct nital.
Images of strained X70 samples in the following sections were compared to the as-received micrographs to assess microstructural changes after straining at various temperatures. Microscopy analysis was complementary to the x-ray diffraction results discussed in Chapter 6. Discussions of all complementary techniques (SEM/TEM, synchrotron WAXS, stress relaxation, internal friction, and strain rate sensitivity measurements) in the PhD work are included in Chapter 9.

1.32 Strained Microstructures

Micrographs discussed in this section were taken from sections of tested tensile samples strained at various temperatures at a strain rate of $10^{-4}$ s$^{-1}$. The samples correspond to the same coupons used for the APS synchrotron WAXS study discussed in Chapter 6. Micrographs were oriented normal to the tensile axis (longitudinal direction). Since the samples were approximately circular, the orientation of the micrographs with respect to the normal and transverse directions was unknown.

Figure 7.2 presents a characteristic SEM micrograph of the X70 steel strained at room temperature to 9.5 pct engineering strain and a slightly higher magnification image with examples of quasi-polygonal ferrite (F), austenite (A), and MA islands. Note that sample orientations of the figures showing strained microstructures were oriented 90° to what was shown in Figure 7.1. Both types of microconstituents hypothesized to be austenite and MA islands were observed in the strained sample. Careful inspection within the ferrite grains indicated that the fine particles hypothesized to be carbides were also observed. Austenite grains, MA islands, and carbide particle sizes were approximately equivalent to what was observed in the as-received material (Figure 7.1). No distinct microstructural differences or phase changes were detected with SEM imaging after straining at room temperature.

Figure 7.3a presents a characteristic SEM micrograph of the X70 steel strained at 202 °C (within the DSA regime) to 7.1 pct engineering strain and a slightly higher magnification image (in Figure 7.3b) with examples of quasi-polygonal ferrite, austenite, and MA islands. The microstructures of the room temperature (Figure 7.1) and 202 °C (Figure 7.3) samples were indistinguishable compared to each other (with respect to the phases present). Austenite, MA islands, and fine particles within the ferrite were all observed in the 202 °C strained microstructure.

Figure 7.4 presents characteristic SEM micrographs of the X70 steel strained at 299 °C to 10.8 pct engineering strain and slightly higher magnification images with examples of quasi-polygonal ferrite and two-phase microconstituents (Figure 7.4c and 7.4d). In contrast to the samples deformed at lower temperatures (shown in Figure 7.2 and 7.3), only two-phase microconstituents were observed in the 299 °C sample (i.e. austenite was no longer observed) in addition to quasi-polygonal ferrite and carbides.
Figure 7.2 Scanning electron micrographs of the X70 steel strained at 25 °C to 9.5 pct engineering strain. Samples were taken from the gauge section of a tested tensile specimen. The tensile axis (longitudinal direction) is oriented normal to the plane of the image, but the normal and transverse directions are unknown (due to the round sample geometry). (a) Characteristic micrograph of a random location on the sample and (b) slightly higher magnification image to show microconstituents. Examples of quasi-polygonal ferrite (F), and microconstituents hypothesized to be austenite (A), and martensite-austenite (MA) islands are indicated in (b). Sample etched with 2 pct nital.

Figure 7.3 Scanning electron micrographs of the X70 steel strained at 202 °C to 7.1 pct engineering strain. Samples were taken from the gauge section of a tested tensile specimen. The tensile axis (longitudinal direction) is oriented normal to the plane of the image, but the normal and transverse directions are unknown (due to the round sample geometry). (a) Characteristic micrograph of a random location on the sample and (b) slightly higher magnification image showing microconstituents. Examples of quasi-polygonal ferrite (F), and microconstituents hypothesized to be austenite (A), and martensite-austenite (MA) islands are indicated in (b). Sample etched with 2 pct nital.
Figure 7.4 Scanning electron micrographs of the X70 steel strained at 299 °C to 10.8 pct engineering strain. Samples were taken from the gauge section of a tested tensile specimen. The tensile axis (longitudinal direction) is oriented normal to the plane of the image, but the normal and transverse directions are unknown (due to the round sample geometry). (a) and (b) Characteristic micrographs of random locations on the sample, (c) and (d) slightly higher magnification images showing microconstituents, and (e) and (f) high magnification images of the two phase microconstituents from (c) and (d). Examples of quasi-polygonal ferrite (F), and microconstituents hypothesized to be austenite (A), martensite-austenite (MA) or decomposed austenite (DA) islands, and carbides (C) are indicated in (c)-(f). Sample etched with 2 pct nital.
It was hypothesized that the austenite grains decomposed (i.e. exhibited at phase change) to ferrite and cementite during straining at approximately 300 °C and higher temperatures. Two-phase microconstituents discussed in Figure 7.4 were classified as either MA islands or decomposed austenite (DA). Regions with decomposed austenite likely consisted of cementite and ferrite phases. Careful inspection of the ferrite grains indicated that the fine randomly dispersed particles (examples of which are indicated as carbides (C) in Figure 7.4e and 7.4f with white arrows), approximately 20-100 nm in diameter, were still present in the 299 °C sample.

1.33 Transmission Electron Microscopy of Carbides

Transmission electron microscopy was used to observe the randomly dispersed fine particles detected within the ferrite grains in SEM (discussed in the previous section). Figure 7.5a shows a selected area diffraction pattern obtained from a (111) zone and (110) g-vector two beam condition in a ferrite grain (also presented in Figure 7.6a). The highest intensity diffraction spots were associated with the diffraction of the ferrite grain. Several low intensity diffraction spots were observed in two-beam condition.

Figure 7.5
(a) Selected-area diffraction pattern of a (110) g-vector two-beam condition in the as-received X70 steel. (b) Simulated two-beam condition with ((110) g) select cementite diffraction spots based on the Isaichev orientation relationship [137]. Ferrite diffraction spots of the two figures are oriented at the same angle relative to each other. The white arrows in (a) indicate the hypothesized cementite diffraction spots.
It was determined that most of the low intensity diffraction spots were associated with iron oxide on the surface of the TEM sample [138]. However, two diffraction spots were hypothesized to be diffraction of cementite particles (indicated by the white arrows in Figure 7.5a). Figure 7.5b shows a simulated two-beam condition diffraction pattern of ferrite and cementite with the Isaichev orientation relationship ([010]Fe₃C//[111]α; (101)Fe₃C//(112)α) [137]. The diffraction spots indicated with the white arrows in Figure 7.5a were at approximately the same location as the simulated Fe₃C(201) and Fe₃C(202) spots.

Figure 7.6 shows the TEM selected area diffraction pattern discussed in Figure 7.5 and bright- and dark-field images of hypothesized cementite particles in the as-received ferrite matrix. Dark-field images were obtained using the diffraction spot near the simulated Fe₃C(201) position, which was indicated by the white circle in Figure 7.6a. Three carbides were observed in the dark-field images (Figure 7.6c and 7.6d) and the locations of the observed carbides are indicated by the black circles in the bright-field image (Figure 7.6b). The carbides were approximately 20-30 nm in diameter, which were slightly smaller than many of the carbides observed in see Figure 7.1. However, the smallest carbides were difficult to observe in the SEM.

Carbides were also observed in the X70 299 °C 10.8 pct sample (recall from Section 4.4 that 299 °C 10⁴ s⁻¹ is outside the DSA regime, and exhibited uniform deformation). Figure 7.7a shows the selected area diffraction pattern of a (110) zone and (200) g-vector two beam condition in a ferrite grain of the strained sample. Figure 7.7b and 7.7c show the bright- and dark-field images associated with a particle found in the ferrite grain. The diffraction spot used for the dark-field image is indicated by the white circle in Figure 7.7a and the location of the particle in the bright-field image is indicated by the black circle in Figure 7.7b. The particle size was approximately 40 nm in diameter (on the same order to what was observed in the SEM in Figure 7.4).

It was hypothesized that the particles observed in Figure 7.7 were cementite. However, more TEM work is required for complete phase, size distribution, and volume fraction analysis of the particles. TEM results suggest that precipitates were present in the quasi-polygonal ferrite grains after straining at all temperatures. Further discussion of the SEM and TEM results are included in Chapter 9.

1.34 Summary of Microscopy Results

Microstructures of strained X70 samples were studied using SEM and TEM. The as-received microstructure consisted of quasi-polygonal ferrite with two microconstituents hypothesized to be austenite and MA islands. Fine particles dispersed randomly within the ferrite grains, hypothesized to be carbides, were also observed in the as-received X70 microstructure. The austenite and MA islands were
typically on the order of 1-2, μm and the carbide particles in the ferrite grains were typically on the order of 30-100 nm in diameter.

Figure 7.6  X70 as-received microstructure. (a) selected-area diffraction pattern of the two-beam condition (200 g) used for the (b) bright-field, (c) and (d) dark-field images showing the observations of carbides in a ferrite grain. Note, image (d) was obtained at a slightly different tilt angle than images (b) and (c), but the dark-field image used the same carbide diffraction spot.
Samples strained at 25 and 202 °C exhibited approximately the same microstructures as the as-received material. However, the sample strained at 299 °C exhibited decomposition of austenite after elevated temperature deformation. The fine particles observed in the ferrite grains were studied using TEM. Electron diffraction analysis of the as-received microstructure suggested that the fine particles in ferrite were likely cementite. However, more analysis is required for complete phase, volume fraction, and size distribution analysis of the particles. Particles were observed after deformation at all temperatures up to at least 300 °C.

![Image](image_url)

**Figure 7.7** X70 microstructure deformed at 299 °C to 10.8 pct engineering strain. (a) selected-area diffraction pattern of the two-beam condition (200 g) used for the (b) bright-field and (c) dark-field images showing the observation of a carbide in a ferrite grain.
CHAPTER 8

INTERNAL FRICTION ANALYSIS

Torsional pendulum internal friction testing was performed to study the effects of elevated temperature deformation on the free interstitial concentrations in the pipeline steels. The following sections include results and discussion of internal friction data in as-received X52 and X70 steels and the influence of deformation temperature on free interstitial carbon concentrations. Note, all internal friction tests in the present study were performed with room temperature-variable frequency measurements. Samples were deformed at elevated temperatures and then tested in the torsional pendulum after cooling to room temperature. Fitting parameters for all internal friction measurements are included in Appendix F. Internal friction analysis was considered a complementary characterization technique to experiments discussed in previous chapters. References to observations presented in previous chapters are included in the internal friction analysis and further discussions of all results relevant to the project objectives are continued in Chapter 9.

1.35 Internal Friction Analysis of As-Received X52 and X70 Steels

Internal friction spectra were generated at room temperature in the frequency range of $10^{-4}$ to 10 Hz. Figure 8.1 shows the internal friction spectra of the as-received X52 and X70 steels. Note that several as-received samples were tested prior to straining at elevated temperatures. The data presented in Figure 8.1a and 8.1b are characteristic spectra of all as-received X52 and X70 experiments respectively. Deconvolutions of the Debye peaks and background were performed using Equation 3.13 for accurate measurements of peak heights ($Q_{Max}^{-1}$). As discussed in Section 3.9, the Debye peaks present in the internal friction spectra must be determined prior to deconvolution. Three nitrogen (N) Snoek, one carbon (C) Snoek, and the $\gamma$-Bordoni internal friction peaks associated with bcc iron were potentially present in the tested frequency range. The three N-Snoek peaks are observed in Fe-Mn systems because nitrogen atoms typically have manganese atoms as nearest neighbors [139]. The N$_0$-, N$_1$-, and N$_2$-Snoek peaks refer to free nitrogen interstitials with zero, one, and two manganese atoms as nearest neighbors respectively.

Table 8.1 shows the activation energies and time constants used to calculate frequencies of the potential Debye peaks for a 25 °C variable frequency internal friction experiment. The theoretical N-Snoek peak locations were indicated as blue dashed lines and the deconvoluted background, C-Snoek, and $\gamma$-Bordoni peaks are plotted in Figure 8.1 for reference. It was determined that only the C-Snoek and $\gamma$-Bordoni peaks were detected in the internal friction spectra for the X52 and X70 steels. The pipeline
steel spectra only exhibited statistically significant peaks at frequencies associated with the C-Snoek and γ-Bordoni theoretical frequencies.

![Internal friction spectra of as-received (a) X52 and (b) X70 steels.](image)

**Figure 8.1** Internal friction spectra of as-received (a) X52 and (b) X70 steels. Internal friction spectra were generated at 25 °C. Error bars indicate the 95 pct confidence intervals of n measurements. The spectra were fit with C-Snoek and γ-Bordoni Debye functions (red lines). The C-Snoek, γ-Bordoni, and background functions were deconvoluted and plotted under the data for reference. The theoretical locations of the three nitrogen peaks are also plotted for reference (blue lines). *(Color image, the reader is referred to the .pdf version of this document)*

The γ-Bordoni peak heights were approximately the same for the X52 and X70 steels, which indicated that both materials exhibited propensities of forming screw dislocation kinks in the ferrite grains to enable dislocation motion. However, Nowick and Berry [93] discussed that fundamental properties of
dislocation lines associated with the Bordoni relaxation are difficult to interpret in bcc and hcp metals. The Bordoni peak height in bcc metals is dependent on the material purity, the torsion amplitude (i.e. the strain imparted on the sample during vibration), the dislocation density, material processing conditions and potentially other sources related to dislocation movement [92, 93]. Nowick and Berry [93] discuss that the α-Bordoni (low temperature internal friction peak associated with edge dislocation kink formation) height decreases in proportion to the work hardening (i.e. the dislocation density) and also decreases with annealing temperature (discussed with respect to results from different studies). Changes in the Bordoni peak height between samples were therefore difficult to relate to specific metallurgical processes or properties and further interpretation of the γ-Bordoni peaks observed in the pipeline steels was not included in the present work.

Table 8.1 – Frequencies for Snoek and γ-Bordoni Peaks at 25 °C [81, 92, 95–104, 106–108]

<table>
<thead>
<tr>
<th>Peak</th>
<th>(Q_i) (eV)</th>
<th>(\tau_0) (s)</th>
<th>Debye Peak Location (Frequency) at 25°C (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_0)-Snoek</td>
<td>0.803</td>
<td>2.04 x 10^{-15}</td>
<td>1.45</td>
</tr>
<tr>
<td>(N_1)-Snoek</td>
<td>0.841</td>
<td>2.04 x 10^{-15}</td>
<td>0.43</td>
</tr>
<tr>
<td>(N_2)-Snoek</td>
<td>0.761</td>
<td>2.04 x 10^{-15}</td>
<td>9.01</td>
</tr>
<tr>
<td>C-Snoek</td>
<td>0.875</td>
<td>1.50 x 10^{-15}</td>
<td>0.15</td>
</tr>
<tr>
<td>(γ)-Bordoni</td>
<td>0.750</td>
<td>4.14 x 10^{-12}</td>
<td>0.008</td>
</tr>
</tbody>
</table>

The height of the C-Snoek peak is directly related to the free interstitial concentration of carbon atoms and the grain size [92]. The C-Snoek peak height was slightly greater in as-received X52 samples compared to X70 samples (e.g. \(Q_{Max,C}\) values in Figure 8.1 were approximately 9.9 x 10^{-5} and 5.4 x 10^{-5} ± 0.6 x10^{-5} in the X52 and X70 steels, respectively). Errors in the C-Snoek peak heights were based off the 95 pct confidence intervals of the data near 0.15 Hz (the theoretical frequency of the C-Snoek peak at 25 °C). It was estimated that the deviation in measured C-Snoek peak height was approximately equal to the average range of internal friction measurements within the 95 pct confidence intervals where the peak was detected. All X52 and X70 experiments exhibited internal friction error values of approximately 6 x 10^{-6}. Differences in grain size of the X52 and X70 steels (approximately 16 and 2.4 μm respectively, refer to Section 3.2) made direct comparisons of free interstitial concentrations between the X52 and X70 steels difficult. Changes in C-Snoek peak heights after deformation are discussed in the next section.

The absence of detectable free interstitial nitrogen in internal friction data supports the hypothesis that approximately all the nitrogen present in the pipeline steels studied here was in the form of nitrides (discussed in Section 3.2). However, recall from the serration maps presented in Section 4.4 and Figure 4.15 that the X52 steel exhibited DSA at lower temperatures compared to the X70 steel (e.g. at 1.67 x 10^{-4} s^{-1}). The low temperature boundaries of the DSA regime were approximately 110 and 139 °C for the X52 and X70 steels respectively. Dynamic strain aging associated with interstitial nitrogen-
dislocation interactions in the X52 steel (and not present in the X70 steel) was hypothesized to be the cause of the differences in the relatively low temperature DSA regimes (based on analysis of the serration maps in Section 4.4). X52 steel tensile data also exhibited yield point elongation (YPE) from static strain aging (for an example, the reader is referred to Figure 4.2). The presence of YPE in the X52 steel indicated that interstitial atoms were trapped at dislocation cores prior to plastic deformation. Recall that Snoek and Snoek-Ké-Koster (SKK) peaks are associated with mechanical dampening from the diffusion of free and trapped interstitial atoms respectively. The SKK peak is also associated with dampening from both carbon and nitrogen interstitials in steels. It was hypothesized that free nitrogen atoms were present and undetected in the X52 room temperature internal friction spectra because the total concentration of interstitial nitrogen atoms was relatively low (due to the presence of nitride forming elements in the chemical composition), and/or most of the nitrogen interstitials were trapped at dislocation cores (supported by the presence of YPE in the tensile data) and contributed to the SKK peak. However, more experimentation is required to analyze the interstitial nitrogen concentrations in the pipeline steels.

### 1.36 Changes in Free Interstitial Carbon After Plastic Deformation

Changes in free interstitial carbon were assessed by comparing room temperature internal friction spectra of as-received and strained samples deformed at various temperatures. Internal friction experiments were performed on each sample before (i.e. the as-received condition) and after approximately 3 pct plastic deformation at various temperatures (target temperatures were approximately 25, 150, 200, and 300 °C; refer to Table 3.6). Figure 8.2 shows the internal friction spectra for the X52 steel in the as-received and 300 °C 3 pct conditions (Figure 8.2a) and the corresponding data for the X70 steel in the as-received 314 °C 3 pct conditions (Figure 8.2b). At all frequencies, the internal friction values of the as-received samples were greater than the internal friction values of the strained samples. The general increase in the internal friction values measured was a result of differences in background dampening between the two conditions (primarily associated with the $\gamma_0$ parameter in Equation 3.13). Examples of the functionality of the background were discussed in the previous section and shown in Figure 8.1. Changes in the background intensities of the torsional pendulum apparatus after straining were associated with the slight sample geometry change after plastic deformation and further emphasized the importance of deconvoluting the C-Snoek dampening from background and $\gamma$-Bordoni dampening to assess changes in free interstitial carbon concentrations after straining at different temperatures. It was also assumed that the grain sizes of each steel remained unchanged after 3 pct prestrain. Total carbon concentrations (0.048 and 0.045 wt pct for X52 and X70 respectively, refer to Table 3.1) were also assumed to be constant before and after pre-straining (i.e. no decarburization occurred during internal friction testing or elevated temperature tensile testing). With constant grain sizes and total carbon
concentrations, changes in the Snoek peak were directly related to changes in free interstitial carbon concentrations in the steels. Therefore, changes in C-Snoek peak heights were inversely proportional to changes in the SKK peak height, except for samples that exhibited phase changes during plastic deformation (i.e. X70 samples strained at temperatures greater than approximately 300 °C; refer to WAXS and SEM results in Chapters 6 and 7).

Figure 8.2 Internal friction spectra of (a) X52 and (b) X70 steels comparing the as-received (AR) and 300 °C 3 pct conditions. Internal friction spectra were generated at 25 °C. Error bars indicate the 95 pct confidence intervals of \( \bar{n} \) measurements. The spectra were fit with C-Snoek and \( \gamma \)-Bordoni Debye functions (red lines). The C-Snoek and \( \gamma \)-Bordoni functions were deconvoluted and plotted under the data for reference (solid and dashed lines for AR and strained samples respectively). The change in C-Snoek peak height (\( \Delta Q_{\text{Max(C)}} \)) is shown schematically in (a). Values indicated as C or \( \gamma \) are the peak heights associated with either the C-Snoek or \( \gamma \)-Bordoni relaxations. (Color image, the reader is referred to the .pdf version of this document)
Wagner et al. [45] showed that the Snoek peak height decreased and the SKK peak height increased after plastic deformation of steels. Plastic deformation results in increased dislocation densities which increase the probability of interstitial atom-dislocation interactions (i.e. the Snoek and SKK peaks decrease and increase respectively). For the example shown in Figure 8.2a, the X52 300 °C 3 pct sample exhibited the same behavior described by Wagner et al. [45]. Specifically, after plastic deformation the C-Snoek peak height decreased relative to the as-received condition, which indicated that there were fewer free interstitial carbon atoms in the ferrite matrix. The decrease in the C-Snoek peak height was assumed to be associated with an increase in the SKK peak height (i.e. the reduction in concentration of free interstitial carbon atoms resulted in an increase in the concentration of trapped interstitial atoms at dislocation cores).

The changes in C-Snoek peak heights were compared for X52 and X70 steels by subtracting the peak height of the as-received sample from the samples strained to 3 pct (indicated schematically in Figure 8.2a, \( \Delta Q^{-1}_{Max(C)} = Q^{-1}_{Max(C),Strained} - Q^{-1}_{Max(C),AR} \)). Figure 8.3 shows the deformation temperature dependence on the \( \Delta Q^{-1}_{Max(C)} \) values for the X52 and X70 steels. The dashed line indicates \( \Delta Q^{-1}_{Max(C)} = 0 \) as a reference for zero change in C-Snoek peak height after plastic deformation. According to the discussion above, \( \Delta Q^{-1}_{Max(C)} \) values should theoretically be less than zero, since the C-Snoek peak height decreases (and SKK peak height increases) after plastic deformation. At room temperature, the X52 and X70 steels exhibited approximately the same decrease in the C-Snoek peak height (within the calculated errors discussed in the previous section), which indicated that the repeatability of the measurements was reasonable.

The changes in the C-Snoek peak heights for samples strained within the DSA regime for the X52 and X70 steels were indicated by the shaded region in Figure 8.3. The lower and higher temperature DSA conditions were selected to study differences in interstitial-dislocation interactions associated with low frequency (propagating type deformation bands) and high frequency serrations (nucleating type deformation bands, refer to Chapter 4) respectively. It was hypothesized that the magnitude of \( \Delta Q^{-1}_{Max(C)} \) values measured within the DSA regime would be greater than the magnitude of \( \Delta Q^{-1}_{Max(C)} \) values measured at room temperature (i.e. \( |\Delta Q^{-1}_{Max(C),25°C}| < |\Delta Q^{-1}_{Max(C),DSA}| \)), due to the relatively larger dislocation densities associated with deformation in the DSA regime (refer to Figure 2.3 [13]). Since X52 and X70 steels exhibited approximately the same localized deformation, strength, and ductility behaviors within the DSA regime (i.e. within the DSA regime, flow stress increased as a function of temperature, ductility was reduced relative to room temperature, and strain rate sensitivities were negative), it was also hypothesized that the \( \Delta Q^{-1}_{Max(C)} \) values would exhibit the same behaviors compared to each other.
The X52 steel exhibited decreased $\Delta Q_{\text{Max}(C)}^{-1}$ values and the X70 steel exhibited slightly increased $\Delta Q_{\text{Max}(C)}^{-1}$ values after 3 pct deformation within the DSA regime (comparison relative to the 25 °C results). The magnitude of the X52 $\Delta Q_{\text{Max}(C)}^{-1}$ values measured within the DSA regime were greater than the values measured at room temperature (which matched the hypothesized behavior discussed above). However, the $\Delta Q_{\text{Max}(C)}^{-1}$ values measured in the DSA regime were within the calculated error compared to each other and the as-received condition (i.e. the error bars overlapped for the three data points in Figure 8.3). The X70 specimens exhibited the opposite trend compared to the X52 samples when tested within the DSA regime. The X70 $\Delta Q_{\text{Max}(C)}^{-1}$ magnitudes were smaller after plastic deformation within the DSA regime compared to samples tested at room temperature. The internal friction results for samples deformed within the DSA regime were therefore inconclusive.

![Figure 8.3](image_url)

Figure 8.3 The effect of deformation temperature on the change in C-Snoek peak height in the X52 and X70 steels. The approximate DSA regime and zero $\Delta Q_{\text{Max}(C)}^{-1}$ are indicated for reference by the shaded region and dashed line respectively. The error bars indicate the range of calculated $\Delta Q_{\text{Max}(C)}^{-1}$ values based on the 95 pct confidence intervals of the internal friction data between 0.08 and 0.6 Hz (the frequency for $Q_{\text{Max}(C)}^{-1}$ at 25 °C is 0.15 Hz).

The X70 sample strained at 314 °C exhibited approximately zero change in C-Snoek peak after 3 pct plastic deformation (internal friction spectra presented in Figure 8.2b). All X52 and lower temperature X70 experiments exhibited a decrease in the C-Snoek peak height after plastic deformation, because higher concentrations of carbon atoms were trapped at dislocation cores. A zero change in
\( \Delta Q_{Max(C)}^{-1} \) value after plastic deformation at 314 °C indicated that the concentration of free carbon interstitial atoms was equivalent in the as-received and strained samples. However, an un-changing Snoek peak height after plastic deformation indicated that either the total interstitial concentration increased, or the dislocation density remained constant. It was hypothesized that the total interstitial carbon concentration in ferrite (free and trapped interstitials) was greater in the strained condition compared to the as-received condition. Recall from the diffraction data presented in Figure 6.8 in Section 6.3, that samples strained at temperatures greater than 300 °C exhibited decomposition of austenite and dissolution of carbides in the X70 microstructure. Prior to austenite decomposition, the concentration of interstitial carbon atoms within ferrite grains was less than the concentration of interstitial atoms in the austenite grains (i.e. carbon has greater solubility in austenite compared to ferrite). Upon the decomposition of austenite, carbon atoms formed carbides and/or increased the total interstitial carbon concentration in the ferrite grains. Carbides also have a higher concentration of carbon than the quasi-polygonal ferrite grains. Dissolution of carbides could also increase the carbon concentration in the quasi-polygonal ferrite. Decomposition of austenite and dissolution of carbides would therefore, theoretically increase both the C-Snoek and SKK peak heights. Further discussions of the high temperature internal friction results are included in Chapter 9.

1.37 Summary of Internal Friction Results

Internal friction analysis of the as-received X52 and X70 steels indicated that C-Snoek and \( \gamma \)-Bordoni peaks were detected in the internal friction analysis. C-Snoek and \( \gamma \)-Bordoni peaks were detected at the temperature and frequency conditions predicted by the Debye relationships using the activation energies and residence times provided by the literature [81, 92, 95–104, 106–108]. The presence of the \( \gamma \)-Bordoni peak in the X52 and X70 steels indicated that both materials exhibited propensities of forming kinks on screw dislocations to cause plastic deformation. Except for the X70 314 °C 3 pct sample, the C-Snoek peak heights in the internal friction spectra were lower in the strained conditions compared to the as-received conditions. Decreases in C-Snoek peak heights were associated with increases in the SKK peak heights, as increased dislocation densities in strained samples resulted in higher probabilities of interstitial-dislocation interactions. The C-Snoek peak heights for the X70 as-received and 314 °C 3 pct conditions were approximately equal compared to each other. It was hypothesized that the decomposition of austenite and dissolution of carbides in the X70 microstructure during deformation at temperatures greater than 300 °C caused an increase in total interstitial carbon concentrations in the ferrite grains, which resulted in an increase in both the C-Snoek and SKK peak heights.
CHAPTER 9

DISCUSSION OF EXPERIMENTAL RESULTS

Previous chapters independently discussed the deformation temperature dependence of strength, ductility, strain rate sensitivity, internal/effective stress, and activation volume on the X70 pipeline steel. Phase, microstructure, and interstitial carbon concentration changes after elevated temperature tensile deformation were also presented. The purpose of this chapter is to discuss key findings of the experimental results pertaining to the characterization of the mechanical properties of X70 line pipe steels (which was the main objective of the PhD work). Data from previous chapters are either reproduced or summarized in this chapter to relate key observations from various experiments to the project objectives (outlined below). References to the chapters where data were first introduced are provided.

It was hypothesized in the MS work [12] that dynamic strain aging (DSA) contributed to a substantial portion of the elevated temperature mechanical behavior in line pipe steels. Therefore, the experiments performed in the MS work were designed to study the influence of DSA on mechanical properties in pipeline steels. Mechanical deformation behaviors associated with DSA (related to the first PhD objective) were also investigated and the results were presented and discussed in Chapter 4. It was found that X70 steels exhibited approximately the same DSA characteristics compared to a control X52 material with known properties (these observations are included in discussions below). However, the temperature dependent properties of the X70 steels exhibited behavior at deformation temperatures greater than the DSA regime (specifically at approximately 300 °C) that warranted further investigation [12]. The second PhD objective was therefore, to identify metallurgical phenomena in the X70 steels that contribute to the mechanical behaviors observed at high temperatures, just outside the DSA regime. Dynamic strain aging, precipitate coarsening, dynamic precipitation of carbides/nitrides, tempering of martensite in MA constituent, bainitic tempering of the quasi-polygonal ferrite microstructure, and strain induced transformation/decomposition of retained austenite were considered to potentially influence the elevated temperature mechanical properties of X70 steels. Changes in the X70 microstructure after elevated temperature deformation were evaluated with microscopy and diffraction techniques and were then compared to mechanical property and defect measurements.

1.38 X70 Steel Microstructure and Phase Changes After Elevated Temperature Tensile Deformation

Changes in the X70 microstructure were evaluated before and after elevated temperature tensile deformation and related to the mechanical properties. Figure 9.1a shows a characteristic micrograph obtained with a scanning electron microscope (SEM) of the as-received X70 microstructure that consisted of quasi-polygonal ferrite with single and two-phase microconstituents, hypothesized to be austenite (A)
and martensite-austenite (MA) islands respectively. Austenite grains appeared smooth and white in the dark ferrite matrix and MA islands had a light and dark two-phase structure with varying morphologies. Both microconstituents were observed at quasi-polygonal ferrite grain boundaries. Figure 9.1b shows a higher magnification SEM micrograph of the X70 steel with fine particles dispersed within the quasi-polygonal ferrite grains. Particle sizes observed in SEM varied from approximately 20-100 nm in diameter. It was hypothesized that the fine particles were iron or microalloy carbides/nitrides (e.g. cementite/Fe₃C or NbC). The particles were investigated further with transmission electron microscopy (TEM) and wide-angle x-ray scattering (WAXS).

![Figure 9.1](image)

(a) Characteristic and (b) high magnification scanning electron micrographs of the as-received X70 steel. Sample orientation is indicated relative to the longitudinal (L), normal (N), and transverse (T) directions. Examples of secondary microconstituents hypothesized to be austenite (A), martensite-austenite (MA), and carbides (C) are indicated with white arrows. Sample was etched with 2 pct nital. Note, these images were first introduced from the sample associated with Figure 7.1.

Figure 9.2 shows the TEM results of carbides detected in the quasi-polygonal ferrite as-received X70 steel microstructure. A selected area diffraction pattern (Figure 9.2a) down the (110) g-vector in a two-beam condition in a random ferrite grain exhibited several secondary phase diffraction spots. Most of the spots observed with electron diffraction were hypothesized to be iron oxide buildup on the TEM foil. However, two spots were hypothesized to be Fe₃C(201) and Fe₃C(201̅) diffraction conditions, which were simulated in Figure 9.2b with the Isaichev orientation relationship [137] in α-iron. The particles were highlighted using dark-field imaging (Figure 9.2d) in the TEM using the Fe₃C(201) diffraction spot. The particles were approximately 20-30 nm in diameter (which was on the order of the particle size observed in the SEM). The bright-field image with locations of the observed carbides was provided in Figure 9.2c for reference. The TEM analysis of carbides in the quasi-polygonal ferrite supported the hypothesis that Fe₃C particles were observed in the SEM images. However, more TEM analysis was required to fully characterize the carbides and/or nitrides present in the X70 microstructure.
Figure 9.2 Summary figure of carbides observed in as-received X70 with TEM. (a) Selected-area diffraction pattern of a (110) g-vector two-beam condition in the as-received X70 steel. Arrows indicate hypothesized Fe₃C diffraction spots. (b) Simulated two-beam condition ((110) g-vector from (a)) with select cementite diffraction spots in ferrite based on the Isaichev orientation relationship [137]. Ferrite diffraction spots of the two figures are oriented at the same angle relative to each other. (c) bright-field image of ferrite grain in (d) showing carbides in dark field using the Fe₃C(201) diffraction spot from (a). Note, these images were introduced in Section 7.2. Note, these figures were reproduced from Figure 7.5 and 7.6.
Figure 9.3 summarizes the key findings of the strained microstructure and secondary phase analysis after elevated temperature deformation. The strained microstructures were evaluated from the gauge lengths of tensile bars tested at various temperatures. Micrographs of the X70 as-received, 202 °C, and 299 °C strained conditions are presented in Figure 9.3a, along with the engineering stress-strain curves for the strained samples. The dashed lines indicate the approximate locations along the stress-strain curves where each micrograph was evaluated. There were no noticeable differences in the quasi-polygonal ferrite grains after tensile deformation at all temperature conditions (refer to Chapter 7 for characteristic micrographs of the strained samples at various magnifications). The micrographs included in Figure 9.3a highlight the changes to the secondary microconstituents observed. The 202 °C sample exhibited DSA, which was evident by the serrations in the stress-strain curve. Microstructural observations in the 202 °C sample were the same for all specimens strained at temperatures less than approximately 300 °C, and exhibited austenite, carbides (both indicated in the 202 °C insert micrograph in Figure 9.3a) and MA islands. Microstructures of the samples strained at temperatures less than 300 °C were indistinguishable from the as-received microstructure. However, changes in the microconstituents were observed at deformation temperatures greater than approximately 300 °C. Only two phase microconstituents and carbides were observed in the 299 °C sample (and samples tested at higher temperatures), which indicated that there were phase changes in the austenite grains after deformation. The two-phase microconstituents in the high temperature sample microstructures were hypothesized to consist of ferrite (or martensite) and cementite.

Diffraction analysis with WAXS complemented the microstructural observations discussed above. Figure 9.3b summarizes the key findings of the x-ray diffraction analysis of strained X70 samples. Note, the strained diffraction patterns in Figure 9.3b were taken from the same samples used in the strained microstructure analysis summarized in Figure 9.3a. Ferrite and austenite phases were detected in the X70 steel and their peaks were indexed in Figure 9.3b. The as-received material (black line) and samples tested at temperatures less than 299 °C (represented by the 202 °C sample and indicated by the blue line) also exhibited low intensity peaks at d-spacings between 2.6-1.6 Å that were hypothesized to be diffraction of carbides/nitrides within the X70 steel. Diffraction of cementite was potentially observed in the TEM (Figure 9.2) analysis, and it was therefore hypothesized that cementite resulted in some of the low intensity peaks observed with WAXS. Some peaks were observed at d-spacings associated with cementite lattice parameters (refer to Figure 6.6 in Section 6.2.1 or Appendix A). However, cementite could not account for all the low intensity diffraction peaks in WAXS. Remaining peaks were hypothesized to be caused by the diffraction of transition carbides or microalloy carbides/nitrides.
Figure 9.3 Summary figure of temperature/strain assisted phase changes detected in the X70 steel. (a) Partial engineering stress-strain curves with associated high magnification scanning electron micrographs and (b) WAXS spectra of X70 202 and 299 °C 10^{-4} s^{-1} tensile samples. Examples of austenite (A), decomposed austenite (DA), and carbides (C) in the as-received (AR) and strained samples are indicated in the micrographs. Dashed lines schematically indicate the approximate locations on the stress-strain curves of each micrograph and WAXS spectra. Ferrite ($\alpha$) and austenite ($\gamma$) peaks are indexed. Note, the data included were introduced in Chapters 1, 6, and 7. (Color image, the reader is referred to the .pdf version of this document)
Samples tested at 299 °C (red line in Figure 9.3b) and greater temperatures exhibited substantial decreases in austenite and carbide/nitride peak intensities. The decreases in peak intensities were hypothesized to be a result of decomposition of austenite and dissolution of transition carbides. Only one low intensity peak was retained (at 1.96 Å) in the WAXS patterns of the high temperature samples. The single remaining low intensity peak at 1.96 Å was hypothesized to be diffraction of cementite, since austenite decomposition likely resulted in two-phase ferrite and cementite microconstituents.

The loss of carbide peaks in the 299 °C sample, suggested by the WAXS analysis potentially contradicted the microstructural observations in Figure 9.3a, as carbides (indicated by the white arrows) were still observed in the quasi-polygonal ferrite grains (note that carbides were also observed in the TEM analysis of high temperature samples, see Section 7.2). It was hypothesized that transition carbides either transformed to a more stable phase (i.e. cementite), or the total volume fraction of carbides in the ferrite grains decreased after deformation at approximately 300 °C. However, more quantitative analyses are required for conclusive results regarding transition carbides.

The microstructure and WAXS analyses indicated that decomposition of retained austenite was observed in strained samples tested at temperatures greater than approximately 300 °C. However, SEM and WAXS analyses discussed in Figure 9.2-9.3 required further experimentation to assess the influence of strain on the austenite decomposition. Figure 9.4 (reproduced from Figure 6.9) shows the WAXS results of scans from the grip (0 pct strain) and gauge (5.1 pct strain) sections of deformed internal friction bars tested at 300 and 350 °C. Both grip and gauge samples were exposed to the same heating histories (approximately 2100 s at temperature), so the strain dependence of austenite decomposition could be assessed. At 300 °C 0 pct strain, the austenite peaks were clearly visible and even high index peaks (i.e. γ(311) and γ(222)) were still observed after heating. The relative intensities of the austenite peaks in the 300 °C 5.1 pct sample were substantially lower than the 300 °C 0 pct sample, where only the γ(111) and γ(220) peaks were observed after elevated temperature straining. The 350 °C 0 pct sample exhibited lower austenite peak intensities compared to the 300 °C 0 pct strain sample, which suggested that partial austenite decomposition was observed while heated to 350 °C (for the duration of the pre-straining test). The austenite peaks in the 350 °C 5.1 pct strain sample diminished in relative intensity compared to the 350 °C 0 pct strain sample. It was concluded that strain was required to assist austenite decomposition in samples tested at approximately 300 °C and the strain dependence on austenite decomposition decreased with increasing temperature. Strain assisted austenite decomposition in the X70 steel starting at approximately 300 °C is considered further with respect to the mechanical property and defect results obtained with tensile and internal friction testing in the subsequent sections.

Austenite decomposition and transition carbide dissolution during isothermal heat treatments are consistent with metallurgical phenomena associated with tempering. Krauss [9] discussed Stage II (the
transformation of retained austenite to ferrite and cementite) and Stage III (the replacement of the transition carbides by cementite and ferrite) tempering in martensite to occur at temperatures between 200-300 °C and 250-350 °C respectively. Bhadeshia [140] discussed that tempering of bainite was associated with the same metallurgical phenomena as tempering of martensite (with respect to the transformation of retained austenite and replacement of transition carbides to ferrite and cementite). However, the tempering of bainite typically occurs at greater temperatures/times compared to martensite because the larger precipitates associated with bainitic microstructures take longer to dissolve.

![Figure 9.4 Partial X70 WAXS spectra showing the effects of temperature and strain on austenite decomposition at temperatures greater than 300 °C. Black and blue curves represent diffraction data measured from the gauge and grip sections of a strained internal friction sample respectively. Data were generated at CHESS. Note, these figures were reproduced from Figure 6.9. (Color image, the reader is referred to the .pdf version of this document)]
Bhadeshia [140] described that tempering of bainitic microstructures containing retained austenite consists of three stages (which were slightly different than the stages of martensitic tempering discussed by Krauss [9]). The first stage (lowest tempering temperatures and times; 350-450 °C [141]) consists of interstitial carbon segregation to defects to form clusters and cementite or transition carbide precipitates. Depending on the material, hardness and yield strength can either increase or decrease slightly during the first stage of tempering [140, 141]. The second stage (intermediate temperatures and times 450-600 °C [141]) consists of excess carbon in the ferrite forming cementite, transition carbides being converted to more stable cementite particles, decomposition of retained austenite, and coarsening of cementite particles. The formation of alloy carbides (with Mo, W, V, and Ti) which causes secondary hardening is also associated with the second stage of bainitic tempering. However, the formation of alloy carbides occurs at relatively higher temperatures than the other stage-two tempering phenomena discussed. If the formation of alloy carbides occurs, secondary hardening results in increased yield strength and hardness [140, 141]. The third stage (highest tempering temperatures and times) consists of spheroidization of carbides, extensive recovery of dislocations, and recrystallization of ferrite plates to equiaxed grains. Hardness and yield strength both decrease substantially after tempering in the third stage [140, 141].

The X70 steels had a quasi-polygonal ferrite microstructure with retained austenite, cementite, and potentially transition carbides. Decomposition of austenite and phase changes associated with the low intensity carbide peaks (arrayed in the quasi-polygonal ferrite grains) occurred at approximately 300 °C. It was assumed that the X70 quasi-polygonal ferrite microstructure exhibited the same tempering responses that were discussed by Bhadeshia [140]. References to bainitic tempering in subsequent discussions refer to reactions related to tempering of the quasi-polygonal ferrite measured in the X70 steel. The strain dependent phase and microstructure changes observed in the WAXS and microscopy analyses were therefore associated with tempering of the bainitic X70 microstructure and are referred to as strain assisted bainitic tempering in subsequent discussions. The decomposition of austenite is discussed in the following sections as an indicator that strain assisted bainitic tempering occurred, since austenite diffraction peaks were easily detected with WAXS when austenite was present in the microstructure. However, since austenite decomposition is associated with intermediate temperatures [140], it was possible that carbon segregation and cementite precipitation (the first stage of tempering) occurred at lower deformation temperatures than approximately 300 °C.

It was hypothesized that mechanical property changes detected during strain assisted bainitic tempering (discussed in the next section) were likely a result of precipitation strengthening by cementite due to the relatively low volume fractions of austenite in the X70 microstructure. Bhadeshia [140] discussed that it is possible for cementite to precipitate at relatively low temperatures by a displacive mechanism (defined by Bhadeshia as a mode of deformation of a parent phase, with the additional
characteristic that the crystallographic structure of that phase is altered when deformed) with only the partitioning of carbon, as iron atoms are supplied by the matrix. Quantification of carbide volume fraction, size, and distribution in the X70 steel after deformation at elevated temperatures is proposed for future work. However, data discussed in the subsequent sections were used to make inferences on the influence of strain assisted tempering on the mechanical properties.

1.39 Deformation Temperature Dependent Pipeline Steel Characteristics

This section includes a summary of the temperature dependent properties of the X52 and X70 steels and a discussion of the implications of the results with respect to furthering fundamental understandings of DSA and strain assisted tempering of the quasi-polygonal ferrite microstructure. The microstructural and phase analyses (in the previous section) were discussed directly with respect to the X70 steel. However, the mechanical and defect properties measured with tensile and internal friction testing required comparisons between the X70 and X52 steels to distinguish the influences from DSA and strain assisted bainitic tempering on the results.

Recall that DSA is defined as the changes in properties of a metal that occur when point defects (interstitial atoms in bcc steels) and dislocations interact during plastic deformation [13]. In steels, carbon and nitrogen interstitials cause DSA in the temperature range of interest. Therefore, DSA contributes to the effective stress (short range stress fields and thermally activated) component of the flow stress. Note, higher dislocation densities associated with DSA can also contribute to increasing the internal stress component of the flow stress. Dynamic strain aging only occurs under specific temperature and strain rate conditions, depending on the diffusivity of the solute atoms and velocity of the dislocations. Manifestations of DSA in steel tensile data include serrated flow (e.g. refer to the 202 °C tensile curve in Figure 9.3a), a peak in the flow stress as a function of temperature, decreased ductility, and negative strain rate sensitivities compared to testing conditions outside the DSA regime [14]. Materials that exhibit DSA deform via stable localized deformation (i.e. localized deformation prior to plastic instability or necking discussed in Chapter 4). In general, it is important to note that deformation bands propagate and nucleate at relatively low and high temperatures within the DSA regime respectively (see Figure 4.15). In steels deformed at temperatures greater than the DSA regime, strain rate sensitivities are typically positive, flow stress decreases, and ductility increases as a function of temperature [15].

Figures 9.5 and 9.6 summarize the temperature dependence of yield strength, flow strength at 0.05 true strain, ductility (reported as uniform elongation), strain rate sensitivity m-values (reported with jump and flow stress measurement methods), internal/effective ($\sigma_i/\sigma^*$) stresses at 5 pct engineering strain, apparent activation volume at 3 pct engineering strain, and the change in C-Snoek peak height after 3 pct engineering strain ($\Delta Q_{\text{Max}(C)}^{-1}$) for the X52 and X70 steels respectively. The strain rate for all data
reported in Figure 9.5 and 9.6 was $10^{-4}$ s$^{-1}$ ($10^{-4}$ to $10^{-3}$ s$^{-1}$ for the strain rate sensitivity m-value measurements). The DSA regime at $10^{-4}$ s$^{-1}$ measured from the serration maps in Figure 4.15 (Section 4.4) is indicated by the blue vertical lines and the approximate minimum temperature where strain assisted austenite decomposition was observed in the X70 steel is identified by the red vertical lines. Horizontal dotted reference lines in Figure 9.5b, 9.5d, 9.6b, and 9.6d indicate zero m and $\Delta Q^{-1}_{\text{MAX}(C)}$ values. In Figures 9.5c and 9.6c, horizontal dotted reference lines indicate room temperature values of $\sigma_{\text{f}}/\sigma^{*}$ and activation volume measurements. Note, the data presented in Figure 9.5 and 9.6 are the key results of the PhD study relative to the main objective of the project. Subsequent figures in this section are presented to support the discussion of the elevated temperature mechanical properties of line pipe steels.

Dynamic strain aging had only slight influences on the yield strength of X52 and X70 steels. Within the DSA regime defined by the serration maps, both steels exhibited slight maxima in yield strength. However, the yield strengths of the pipeline steels at elevated temperatures were less than the room temperature conditions. At relatively high temperatures outside the DSA regime, both steels exhibited decreasing yield strength as a function of temperature. The X70 steel retained its high temperature yield strength better than the X52 steel. At 350 °C, the X70 and X52 steels lost approximately 9 and 21 pct of their room temperature yield strengths respectively.

Flow stress measurements at 0.05 true strain were more substantially influenced by DSA for both steels (i.e. between the vertical blue lines in Figure 9.5 and 9.6). Within the DSA regime, the X52 and X70 steels exhibited increasing flow strengths as a function of temperature. Recall from the discussion above (and Chapter 4) that the deformation behavior within the DSA regime was deformation band propagation at relatively low temperatures and nucleation at relatively high temperatures. The increasing flow stress with respect to temperature within the DSA regime indicated that there was a correlation between strengthening from DSA and the deformation band behavior. Specifically, the steels exhibited the greatest strengthening from DSA when tested near the upper bound (and deformation band nucleation regions) of the serration maps.

The X52 and X70 steels exhibited maximum elevated temperature flow strengths at approximately 254 °C and 326 °C respectively. The maximum flow strength for the X52 steel was at approximately the upper bound of the DSA regime. At higher temperatures, the flow stress decreased as a function of temperature (characteristic of behaviors described in the literature [15]). At temperatures greater than the DSA regime and prior to detected strain assisted austenite decomposition, the X70 flow stress increased as a function of temperature. The differences in the temperature dependent flow stress between the X52 and X70 steels at temperatures above the DSA regime suggested that strain assisted bainitic tempering affected the X70 steel at temperatures below the austenite decomposition condition (red vertical line in Figure 9.6).
Figure 9.5 X52 summary figure of the deformation temperature dependence of (a) yield stresses (0.2 pct offset YS), flow stresses at 0.05 true strain ($\sigma_{0.05}$), uniform elongations (UE), (b) strain rate sensitivities (with jump test and $\dot{\varepsilon}_{0.05}$ analysis methods), (c) internal and effective stresses ($\sigma_i/\sigma^*$), apparent activation volumes ($V_{app}$) normalized by the Burgers vector, and (d) change in C-Snoek peak heights ($\Delta Q^{-1}_{Max(C)}$) in the X52 steel. Strain rates for all experiments were $10^{-4}$ s$^{-1}$ ($10^{-4}-10^{-3}$ s$^{-1}$ for m-value measurements). Vertical solid blue and red lines indicate the DSA regime at $10^{-4}$ s$^{-1}$ based on the X52 serration map and the minimum temperature for X70 austenite decomposition ($\gamma$-decomp), respectively. The DSA regime at $10^{-3}$ s$^{-1}$ was included in (b) for reference (vertical blue dashed lines). Horizontal black dotted reference lines indicate zero m-value, zero $\Delta Q^{-1}_{Max(C)}$, and stress relaxation parameters at 25 °C. Internal friction spectra used to measure C-Snoek peaks and calculate ($\Delta Q^{-1}_{Max(C)}$) were generated at 25 °C. Note, the data included were introduced in Chapters 1, 4, 5, and 8. (Color image, the reader is referred to the .pdf version of this document)
Figure 9.6 X70 summary figure of the deformation temperature dependence of (a) yield stresses (0.2 pct offset YS), flow stresses at 0.05 true strain ($\sigma_{0.05}$), uniform elongations (UE), (b) strain rate sensitivities (with jump test and $\sigma_{0.05}$ analysis methods), (c) internal and effective stresses ($\sigma_i/\sigma^*$), apparent activation volumes ($V_{\text{app}}$) normalized by the Burgers vector, and (d) change in C-Snoek peak heights ($\Delta Q^{-1}_{\text{Max}(C)}$) in the X70 steel. Strain rates for all experiments were $10^{-4}$ s$^{-1}$ ($10^{-4}$ to $10^{-3}$ s$^{-1}$ for m-value measurements). Vertical solid blue and red lines indicate the DSA regime at $10^{-4}$ s$^{-1}$ based on the X70 serration map and the minimum temperature for austenite decomposition ($\gamma$-decomp), respectively. The DSA regime at $10^{-3}$ s$^{-1}$ was included in (b) for reference (vertical blue dashed lines). Horizontal black dotted reference lines indicate zero m-value, zero $\Delta Q^{-1}_{\text{Max}(C)}$, and stress relaxation parameters at 25 °C. Internal friction spectra used to measure C-Snoek peaks and calculate ($\Delta Q^{-1}_{\text{Max}(C)}$) were generated at 25 °C. Note, the data included were introduced in Chapters 1, 4, 5, and 8. (Color image, the reader is referred to the .pdf version of this document)
As discussed above, the first stage of strain assisted bainitic tempering was possible at temperatures just below the detected austenite decomposition temperature. Precipitation of cementite particles during deformation at temperatures above the upper bound of the DSA regime potentially occurred in the X70 microstructure to increase the flow stress. The potential precipitation of cementite at deformation temperatures just below 300 °C was supported by the stress relaxation results presented in Figure 9.6c (discussed in detail below).

Strain assisted austenite decomposition was observed at temperatures just below the maximum flow strength for the X70 steel. Recall that austenite decomposition is related to the second stage of bainitic tempering [140]. Also associated with the second stage of bainitic tempering are the dissolution of transition carbides (observed in the WAXS results outlined in Figure 9.3b), coarsening of cementite, and precipitation of alloy carbides for secondary hardening. Since maximum flow stress occurred at approximately the same temperature as strain assisted second stage bainitic tempering (i.e. the flow stress began to decrease as a function of temperature) the total carbon concentration of the X70 steel was relatively low, and new precipitate peaks were undetected in WAXS, secondary hardening from alloy precipitates (discussed above) was unlikely in the X70 steel. Therefore, coarsening of the cementite particles during the second stage of tempering potentially resulted in the decreased flow stress at the highest temperature conditions observed in the X70 steel.

Both steels exhibited reduced ductility within the DSA regime compared to lower and higher temperature testing conditions and the decreased ductility appeared to be independent of the temperature within the DSA regime. At relatively high temperatures, outside the DSA regime, the X52 steel exhibited increasing ductility as a function of temperature and the X70 steel exhibited a maximum in ductility at approximately 275 °C. Just outside the DSA regime, the X70 steel exhibited increasing ductility as a function of temperature (like X52 behavior). Then, at approximately 300 °C (and the strain assisted austenite decomposition condition), the ductility of the X70 steel decreased. Increased precipitation strengthening from strain assisted bainitic tempering processes was potentially associated with the decrease in the X70 ductility in the temperature range of 300-350 °C (due to relationships between strength from precipitates and their influence on strain hardening rate and plastic instability) [43].

It was hypothesized that the precipitation of cementite associated with strain assisted bainitic tempering resulted in increased strength and decreased ductility of the X70 steel, due to the precipitation of cementite at temperatures between 250 and 350 °C (as discussed above). The formation of cementite and austenite/transition carbide decomposition to ferrite and cementite are diffusion based processes and therefore require time to occur. Assuming the decomposition of austenite and transition carbides to form ferrite and cementite increased the flow stress (via precipitation strengthening) at temperatures greater than approximately 250 °C, strain rate sensitivities during strain assisted bainitic tempering would
theoretically be negative, as lower strain rates would allow more time for precipitation of cementite to occur.

Strain rate sensitivity m-values were measured using jump test and flow stress methods. Jump test m-values are a measure of the instantaneous strain rate sensitivity of a material and typically produce more repeatable values than flow stress m-values due to statistical deviations between samples when using the flow stress method (i.e. jump tests use only one specimen and flow stress tests use multiple specimens). However, both experiments are still useful because the quasi-static tensile tests can produce different dislocation substructures compared to the jump tests. Quasi-static tensile tests also may allow sufficient time for certain diffusion based processes to occur during deformation, which may be limited for the jump test due to the cycling of strain rates. Flow stress strain rate sensitivity is therefore more of a measurement of the overall strain rate sensitivity, since m-values are directly related to the strength properties measured from stress-strain curves.

For the X52 and X70 steels, jump test m-values (black symbols in Figure 9.5b and 9.6b) were negative during DSA (for either strain rate used in the measurement) and transitioned to positive at approximately the upper bound of the $10^{-3}$ s$^{-1}$ DSA regime (blue dashed lines). Positive jump test strain rate sensitivities were observed at all elevated temperatures above the $10^{-3}$ s$^{-1}$ DSA regime for both steels. Flow stress strain rate sensitivities (white symbols in Figure 9.5b and 9.6b) for the X52 and X70 steels were also negative for testing conditions that exhibited DSA. The X52 steel exhibited increasing strain rate sensitivities as a function of temperature from 100 to 350 °C, with a transition from negative to positive m-values between 250 and 325 °C (slightly higher temperatures than what were observed in the jump test data). In contrast, the X70 steel exhibited decreasing strain rate sensitivities as a function of temperature from 100 to 325 °C with a transition from negative to positive m-values between 325 and 400 °C. It was hypothesized that DSA affected both the instantaneous and overall strain rate sensitivity measurements, which was why negative m-values were measured with both testing methods. However, tempering of bainite in the X70 steel only affected the overall strain rate sensitivity measurements (i.e. the flow stress method m-values).

The X70 350 and 400 °C flow stress m-values were greater (i.e. negative/closer to zero and positive for the two samples respectively) than the m-values measured in the lower temperature tests. Recall from Figure 9.4 that there was a strong strain dependence on the decomposition of austenite at 300 °C (i.e. strain was required for bainitic tempering), and at 350 °C partial austenite decomposition was observed in the grip section (0 pct strain) of the sample. As discussed above, austenite decomposition was considered an indicator of tempering of the quasi-polygonal ferrite microstructure. The austenite volume fractions were relatively low and decomposition to ferrite and cementite specifically from the austenite islands likely contributed to an insignificant amount of the flow stress. It was hypothesized that complete
austenite decomposition and thus, coarsening of cementite precipitates was possible in the X70 steel without strain when heated at 350 °C for a sufficiently long period of time. Theoretically, the flow strength could decrease as a consequence of cementite particles coarsened with isothermal heat treatments prior to elevated temperature deformation. A hypothetical X70 specimen heat treated at 350 °C for long enough time to decompose the austenite in the microstructure, then tested for strength and strain rate sensitivities at temperatures above the DSA regime could theoretically exhibit reduced flow stresses and positive m-values (comparable to what was observed in the X52 steel). The degree of austenite decomposition was assumed to be related to the coarsening of cementite particles. Partial austenite decomposition was observed (based on the WAXS analysis presented in Figure 9.4) for the X70 350 °C specimens during the 1200 s soak time prior to tensile testing (refer to the experimental procedure for tensile testing in Section 3.4). Partial austenite decomposition prior to deformation at temperatures greater than 350 °C could explain why the flow strength began to decrease and flow stress m-values began to increase as a function of temperature for testing conditions greater than 325 °C. It was possible that more complete austenite decomposition (and substantial cementite coarsening) was observed in the X70 400 °C testing conditions prior to deformation where positive strain rate sensitivities were observed.

Data from the low temperature aging (LTA) study in the MS work (refer to Section 1.1) [12] was compared to the as-received tensile data to estimate the impact of strain assisted bainitic tempering at temperatures greater than approximately 300 °C on the stress-strain curve. Figure 9.7 summarizes temperature dependence of the yield strength, ultimate tensile strength (UTS), and ductility (reported as uniform and total elongations) results for as-received and LTA X70 samples tested at a strain rate of 8 x 10^{-4} s^{-1}. Recall that LTA samples were exposed to the testing temperature (i.e. sample tested at 350 °C was aged at 350 °C) for 100 h under a tensile load of 419 MPa. It was concluded that after extended times at elevated temperatures, static strain aging caused an increase in the yield strength (which was evident by YPE in all LTA tensile curves). Samples tested in the LTA conditions at 200, 275, and 350 °C, respectively, exhibited increased, approximately equivalent, and decreased flow strength and UTS values compared to the as-received samples respectively. Ductility was unaffected by the LTA experiments.

The 350 °C LTA samples were of interest regarding the influences of strain assisted bainitic tempering on the mechanical properties of X70 steels. Recall from Figure 9.4b that partial austenite decomposition was observed in the 350 °C 0 pct strain WAXS results. The data introduced in Figure 9.4b came from the grip and gauge sections of an internal friction sample exposed to elevated temperatures for approximately 1800 s while heating and being strained to 5.1 pct. Since partial austenite decomposition was detected after a relatively short time, the X70 350 °C LTA sample (which was aged for 100 h) was hypothesized to exhibit complete austenite decomposition (and potentially substantial cementite coarsening) prior to plastic deformation at 350 °C. Therefore, a comparison between the as-received and
LTA tensile data was used to estimate the influence of strain assisted bainitic tempering at 350 °C on the X70 mechanical properties. Figure 9.8 shows the true stress-strain curves for the as-received and LTA comparison. The horizontal red dashed line is a reference to the 419 MPa applied stress during the LTA heat treatment. The increased yield strength in the LTA sample was observed with the presence of YPE due to static strain aging. However, the LTA sample exhibited decreased strain hardening rates (i.e. the slope of the true stress-strain curve) at all strains, which resulted in decreased flow stresses greater than 0.01 true strain. It was hypothesized that the greater strain hardening rates of the as-received sample were a result of the strain assisted bainitic tempering of the X70 microstructure. The LTA sample, which theoretically experienced complete austenite decomposition and substantial cementite coarsening prior to plastic deformation, exhibited decreased flow strengths. Strain assisted bainitic tempering was thought to increase the flow stress by precipitating fine carbides dynamically during plastic deformation. If the fine carbides precipitate and coarsen prior to deformation, the flow stress decreases.

![Figure 9.7](image)

**Figure 9.7** Summary figure of the influence of temperature on (a) yield and ultimate tensile strength and (b) elongation measurements in X70 for as-received and LTA tensile testing conditions [27]. Closed shapes indicate as-received tensile samples and open shapes indicate LTA samples. Note, these figures were reproduced from Figure 1.9.

The LTA experiments at 350 °C (discussed above) indicated that strain assisted bainitic tempering influenced the strain hardening rates of the X70 steel at elevated temperatures. For further discussion, a strain hardening rate parameter was developed by calculating the yield strength to flow stress ($\sigma_{0.05}$) ratio at each temperature (data presented in Figure 9.5a and 9.6a). Figure 9.9 shows the

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temperature dependence of the strain hardening parameter (YS/σ0.05) for the X52 and X70 steels. Note, a decrease in the strain hardening parameter indicates an increase in the strain hardening rates observed in the tensile curves (referenced in Figure 9.9). The X52 and X70 steels exhibited a decrease in the strain hardening parameter as a function of temperature within the DSA regime (indicated by the blue lines). At higher temperatures (outside the DSA regime) minima in the strain hardening parameter were observed for both steels. Minimum strain hardening parameters were observed at approximately 275 and 350 °C for the X52 and X70 steels respectively. The X70 steel was hypothesized to exhibit higher strain hardening rates at temperatures greater than approximately 300 °C due to strain assisted bainitic tempering during plastic deformation. Dynamic cementite precipitation during plastic deformation was considered the primary contributor to the increased strain hardening rates. The strain hardening parameter increased for the 400 °C condition because it was hypothesized that cementite precipitation and coarsening occurred during the 1200 s soak time prior to plastic deformation (i.e. cementite could no longer precipitate dynamically during deformation to result in increased strain hardening rates).

![True stress-strain curves for as-received (AR) and LTA X70 tensile specimens](image)

Figure 9.8 True stress-strain curves for as-received (AR) and LTA X70 tensile specimens [27]. The dashed line indicates the applied stress level during the 100 h low temperature age. Note, the data included were introduced in Section 1.1. *(Color image, the reader is referred to the .pdf version of this document)*

The temperature dependence on the stress relaxation parameters was summarized in Figure 9.5c and 9.6c. Internal and effective stress components of the flow stress were plotted from data measured at approximately 5 pct engineering strain and apparent activation volumes were measured at approximately 3 pct strain. Stress relaxation parameters measured at elevated temperatures were compared to room
temperature conditions which were indicated by the horizontal dotted lines in Figure 9.5c and 9.6c. For further discussion of the stress relaxation data, Figure 9.10 (reproduced from Figure 5.7) shows the internal and effective stress measurements normalized by the flow stress (discussed in Section 5.2). Normalized internal/effective stresses are essentially a measure of the fraction of the flow stress influenced by long and short-range stress fields respectively.

Figure 9.9 The temperature dependence on the strain hardening parameter (YS/σ0.05) for X52 and X70 steels tested at 10⁻⁴ s⁻¹. The strain hardening parameter is inversely related to the strain hardening rate (i.e. the slope of the true stress-strain curve). Vertical blue and red lines indicate the DSA regimes (dashed for X52 and solid for X70) and the minimum temperature for austenite decomposition (in X70) respectively. (Color image, the reader is referred to the .pdf version of this document)

The X52 steel exhibited greater effective stress and smaller internal stress at 245 °C (at the upper bound of the DSA regime indicated by the vertical blue line in Figure 9.5c and 9.6c) compared to the room temperature results. The increased effective stress measured near DSA conditions supported the hypothesis that DSA contributed to the effective stress (i.e. short-range stress fields) component of the flow stress as there were strong dislocation-interstitial atom interactions associated with DSA. At higher temperatures outside the DSA regime, the X52 exhibited internal and effective stress that were approximately equal to what was measured at room temperature. In contrast, the X70 steel exhibited decreased effective stresses and increased internal stresses (relative to the room temperature conditions) when tested at temperatures around the strain assisted austenite decomposition condition (approximately 300 °C). The increased internal stress indicate that long range stress fields (i.e. dislocation interactions or
precipitate strengthening) had a greater contribution to the flow strength during testing conditions for strain assisted tempering of the X70 microstructure. Therefore, the internal/effective stress results support the hypothesis that precipitation of cementite was associated with strain assisted bainitic tempering and resulted in increased strength of the X70 steel at deformation temperatures greater than the DSA regime.

Figure 9.10 Summary figure of internal and effective stresses ($\sigma_i/\sigma^*$) normalized by the flow stress ($\sigma_{0.05}$) as a function of engineering strain for the (a) X52 and (b) X70 steels. Note, these figures were reproduced from Figure 5.7.

Schoeck and Seeger [81] showed that the effective stress decreased in iron containing carbon and nitrogen interstitials at temperatures greater than the DSA regime (refer to Figure 2.14a). It was possible that the decrease in effective stress in the X70 steel was associated with the elevated temperature testing conditions. Recall that the effective stress (thermal component of the flow stress) decreases as a function of temperature. At temperatures greater than the DSA regime, Schoeck and Seeger [81] showed approximately zero effective stress in Fe-C-N alloys. However, the X52 data exhibited approximately constant effective stresses at high temperatures compared to the low temperature conditions. More testing is required to investigate the repeatability of the effective stress measurements observed for the pipeline steels at elevated temperatures.

The modified Williamson-Hall analysis performed on the X70 WAXS data (obtained from APS) supported the observations of greater internal stresses at elevated temperatures compared to room temperature. Figure 9.11 summarizes the temperature dependence on the relative dislocation densities obtained from the modified Williamson-Hall analysis (presented originally in Section 6.3). Note that the strain in each measurement was dependent on the uniform elongation since WAXS scans were obtained from tested tensile bars. Samples tested within the DSA regime exhibited greater dislocation densities
than the room temperature sample. Relatively high dislocation densities generated during DSA compared to room temperature conditions corroborated Leslie’s [13] findings outlined in Figure 2.3 (Section 2.2).

At elevated temperatures outside the DSA regime, dislocation densities in the X70 steel were even greater than measurements at both room temperature and DSA conditions.

![Figure 9.11 Summary figure of the Williamson-Hall dislocation density measurements as a function of testing temperature from the APS WAXS results. Strains (indicated above data points) varied between samples and were approximately equal to the uniform elongation (UE). Note, the data included were introduced in Section 6.3 and theis figure was reproduced from Figure 6.10.](image)

The relatively high dislocation densities measured at high temperatures indicated increased dislocation-dislocation interactions which were hypothesized to result in increased internal stresses and strain hardening rates in the X70 steel (observed in Figures 9.6c and 9.9). The potential precipitation of cementite from tempering also could contribute to elevated internal stresses observed in the X70 300 and 350 °C stress relaxation samples. It is possible that an increase in volume fraction of precipitates, and therefore dislocation pinning sites to promote dislocation multiplication through Frank-Reed sources [60], could be directly related to the relatively high dislocation densities and high strain hardening rates observed outside the DSA regime.

Recall that the activation volume (plotted as a function of temperature at 3 pct engineering strain in Figure 9.5c and 9.6c for the X52 and X70 steels respectively) is an indication of deformation mechanisms in metals. It was discussed in Chapter 6 that screw dislocation kink pair migration was
detected in the stress relaxation results for both X52 and X70 steels due to the primarily bcc crystal structure and activation volumes on the order of 10-100b³. Observations from the literature [84, 85] indicate that additions of solid solution strengthening atoms increase the activation volume. Apparent activation volumes for the X52 steel exhibited approximately constant behavior as a function of strain for all temperatures analyzed. The approximately constant apparent activation volumes as a function of temperature at constant strain in the X52 steel were highlighted in Figure 9.5c, where there were less than 5b³ differences in apparent activation volume measurements for the elevated temperature samples. Apparent activation volume measurements for the X70 steel were less than 5b³ for the 25 and 245 °C samples. However, the 297 and 339 °C samples exhibited an increase in apparent activation volume of approximately 20b³ compared to the lower temperature conditions.

The increase in activation volumes at 297 °C and higher temperatures were hypothesized to be associated with increased levels of interstitial carbon concentrations from austenite decomposition and transition carbide dissolution associated with strain assisted bainitic tempering. Recall that microscopy and WAXS results discussed in the previous section indicated that austenite and transition carbides decomposed during straining at temperatures greater than approximately 300 °C (and without strain at temperatures greater than approximately 350 °C) to form ferrite and cementite. Austenite and transition carbides have greater carbon concentrations compared to ferrite crystals (evident by the iron-carbon phase diagram [60]). Dissolution of cementite and transition carbides therefore, can theoretically introduce new interstitial carbon atoms into the ferrite matrix depending on the relative volume fraction of cementite formed upon dissolution. It was discussed above that activation volumes increase in bcc metals when strong solid solution strengthening atoms are present to interact with the screw dislocation kink pairs. It was hypothesized that upon bainitic tempering of the X70 microstructure, the interstitial carbon concentration in the ferrite grains increased, which resulted in an increase in the activation volume.

Internal friction testing was used to test the hypothesis of increased carbon interstitials in the ferrite microstructure after strain assisted bainitic tempering. The results of the internal friction analysis are summarized in Figure 9.5d and 9.6d, which show the change in the C-Snoek peak height (which is directly related to the free interstitial carbon concentration in bcc ferrite) after 3pct deformation for X52 and X70 samples respectively. Theoretically, the C-Snoek peak height is reduced with increased plastic strain, as the dislocation density increases and results in higher probabilities for interstitial-dislocation interactions (that contribute to the SKK peak). The C-Snoek peak height decreased for all X52 and X70 samples tested at room temperature and elevated temperatures, except for the X70 314 °C sample, which exhibited approximately zero change in the C-Snoek peak height. It was assumed that the total carbon concentration (carbon as interstitials and carbides) in the X70 steel was constant for the as-received and strained internal friction experiments (i.e. no decarburization occurred during testing or straining). A
constant C-Snoek peak height after plastic deformation indicated that the interstitial concentration of carbon atoms in the ferrite was greater in the strained sample compared to the as-received X70 steel. The increase of the interstitial carbon concentration detected with internal friction supported the hypothesis that this increase was due to the decomposition of austenite and dissolution of transition carbides.

1.40 The Influence of Dynamic Strain Aging and Strain Assisted Bainitic Tempering on the Mechanical Properties of X70 Steels

It was concluded that DSA and strain assisted bainitic tempering of the quasi-polygonal ferrite microstructure contributed to the mechanical properties of X70 pipeline steels in the temperature range of 100-350 °C. Microstructural, mechanical property, and defect characterization were performed with electron microscopy, wide-angle x-ray scattering, elevated temperature tensile testing, strain rate sensitivity jump testing, stress relaxation testing, and internal friction testing.

Observations of DSA in the mechanical property results of X70 steels exhibited expected behaviors based on discussions from Leslie [13, 14, 38] and Rodriguez [15]. At engineering strain rates of $10^{-4}$ to $10^{-3}$ s$^{-1}$, DSA occurred at relatively low temperatures and was associated with interstitial-dislocation interactions during plastic deformation. Manifestations of DSA relative to room temperature properties include:

1. Serrated yielding and stable localized plastic deformation (characterized in Chapter 4).
2. Increased effective stress which resulted in increased flow stress.
3. Increased strain hardening rates.
4. Decreased ductility.
5. Negative strain rate sensitivities.
6. Increased relative dislocation densities after deformation.

Strain assisted bainitic tempering was defined as austenite decomposition and transition carbide dissolution into ferrite and cementite phases and was first detected in X70 samples strained at temperatures greater than approximately 300 °C. The decomposition of austenite was detected with electron microscopy and synchrotron x-ray diffraction techniques and dissolution of potential transition carbides was associated with the loss of the very low intensity peaks in WAXS line scans. Manifestations of strain assisted bainitic tempering relative to properties measured at lower temperatures (i.e. room temperature and DSA temperatures) include:

1. Increased internal stress from cementite precipitation and relatively high dislocation densities, resulting in increased flow stress (which formed a maximum at approximately 325 °C).
2. Increased strain hardening rates.
3. Decreased ductilities (which had a maximum at approximately 275 °C).
4. Negative overall strain rate sensitivities (i.e. measured with the flow stress method).
5. Positive instantaneous strain rate sensitivities (i.e. measured with the jump test method).
6. Increased interstitial carbon concentrations from the decomposition of austenite and
dissolution of transition carbides (suggested by internal friction C-Snoek peak measurements).
7. Increased apparent activation volumes from kink pair migration in the bcc quasi-polygonal ferrite.

Bainitic tempering of the X70 microstructure was detected at 350 °C without strain. However, austenite decomposition and potentially cementite coarsening were accelerated in deformed samples compared to heated samples. The influence of strain assisted bainitic tempering on the mechanical properties was limited to material that was exposed to temperatures less than 350 °C for extended durations. Decomposition of austenite and coarsening of cementite prior to plastic deformation at temperatures above 300 °C (potentially observed in the low temperature aging study at 350 °C) resulted in decreased strain hardening rates and flow stresses compared to the as-received material.

1.41 Design Ideas and Applications for the use of Bainitic Steels at Elevated Temperatures

With a fundamental understanding of dynamic strain aging and strain assisted bainitic tempering in X70 steels as a base, the next step in the design process is to develop methods of controlling the elevated temperature mechanical behavior. This section is intended to provide ideas for material design and operating conditions for elevated temperature use with steels that exhibit DSA and strain assisted bainitic tempering. The primary focus of this section is for design ideas associated with elevated temperature pipeline applications. However, some other suggestions regarding material forming under DSA conditions are also provided at the end of the section.

1.41.1 Design of a Theoretical X70 Alloy for Elevated Temperature Applications

It was theorized that the strain assisted precipitation of cementite at temperatures slightly greater than the DSA regime contributed to increasing the flow strength. At temperatures just outside the DSA regime, interstitial carbon atoms theoretically contribute less to the flow strength and the addition of new cementite particles from strain assisted bainitic tempering works to increase the internal stress component. It is important to allow the formation of cementite if additional elevated temperature strength is desired. However, the coarsening of cementite associated with the second stage of tempering (indicated by observed austenite decomposition) resulted in reduced flow stresses (see flow stress results above 300 °C
in Figure 9.6a). Alloying the pipeline steels to retard the cementite coarsening process is therefore desired.

Krauss [9] discussed that strong carbide forming elements (e.g. Mo, W, V, Ti, and Cr) exhibit retardation of softening during the early stages of tempering by slowing the cementite coarsening process. Strong carbide forming elements also exhibit secondary hardening by precipitating carbides during tempering at high temperatures. It was determined that the temperatures studied in the present work were too low to accommodate alloy carbide precipitation. However, the influences of carbide forming elements on retarding cementite coarsening were investigated further. Irvine and Pickering [141] performed an extensive study on the effects of alloying elements on tempering responses in low carbon bainitic and martensitic steels. Table 9.1 summarizes the minimum desired alloy concentrations of select carbide forming elements to achieve reductions in softening from cementite coarsening in bainitic steels based on Irvine and Pickering’s work [141].

Other alloying elements have been shown to retard softening in the early stages of tempering. Figure 9.12 shows the effect of several alloying elements on the retardation of softening during early stages of tempering relative to martensitic Fe-C alloys. Nickel has a very slight effect on the retardation of cementite coarsening. It was theorized by Krauss [9] that the retardation associated with nickel was due to solid solution strengthening effects, since nickel does not form carbides in steels. Manganese strongly retards the coarsening of carbides at concentrations greater than approximately 1.25 wt pct because of the incorporation of manganese atoms into cementite. Carbide coarsening when manganese atoms are present in cementite can be limited to manganese diffusion to the ferrite-cementite phase boundary [9]. Silicon has a substantial retardation effect on cementite coarsening which is attributed to its inhibition of the transformation of the low temperature transition carbide to cementite [9].

### Table 9.1 - Minimum Desired Concentrations of Carbide Forming Elements to Retard Softening During Tempering of Bainitic Steels [141]

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>Minimum Desired Concentration (wt pct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0.5</td>
</tr>
<tr>
<td>W</td>
<td>1.0</td>
</tr>
<tr>
<td>V</td>
<td>0.1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.5</td>
</tr>
</tbody>
</table>

A theoretical X70 alloy intended for elevated temperature environments (referred to as ET-X70) was developed to optimize elevated temperature strength based on DSA and strain assisted tempering fundamentals discussed in this chapter. The chemical composition of the theoretical ET-X70 alloy was based on the X70 steel studied in the present work, with additions of select alloying elements intended to
decrease the susceptibility to cementite coarsening at elevated temperatures. Table 9.2 shows partial chemical compositions for the X70 and ET-X70 (proposed composition) alloys. Carbon, manganese, silicon, and niobium contents were held constant while chromium, molybdenum, titanium, and vanadium (carbide forming elements) concentrations were increased. The nickel concentration was reduced in the ET-X70 alloy (to the concentration used in for the other two X70 steels from the MS thesis [12]), because it only had a slight influence on the retardation of cementite precipitate coarsening. It was hypothesized that manganese and silicon concentrations were already high enough to aid the retardation of cementite coarsening. Increasing the silicon content was undesirable because silicon suppresses the formation of cementite particles [9]. A potential modification to the ET-X70 alloy is to reduce the silicon concentration slightly to promote the formation of cementite particles. Increased concentrations of the carbide forming elements were intended to greatly retard the coarsening of cementite during elevated temperature operations and straining at elevated temperatures. Theoretically, the additions of the carbide forming elements would result in greater elevated temperature flow strengths from strain assisted bainitic tempering compared to the X70 steel tested in the present work.

Figure 9.12 Effect of alloying elements on the retardation of softening during tempering of martensite at 260 °C (500 °F) relative to Fe-C alloys [9].

Other considerations are required for the design of the ET-X70 alloy. First, the susceptibility of the ET-X70 alloy to DSA must be assessed, because the increased concentrations of carbide forming elements will likely reduce the interstitial concentrations of carbon in the ferrite matrix. Dynamic strain aging provides substantial strengthening at elevated temperatures up to approximately 250 °C. Therefore,
processing the ET-X70 steel to maintain significant levels of interstitials is desirable. Elevated
temperature tensile testing and internal friction testing of as-received ET-X70 and comparing the results
to the X70 steel (refer to Chapter 8) can indicate the ET-X70 steels susceptibility to DSA. A higher Snoek
peak height theoretically indicates that strengthening from DSA will increase [45]. Experimentation
regarding the influence of various processing conditions (i.e. hot rolling temperatures, deformation
schedules, and coiling temperatures) on interstitial concentrations (and thus the maximum strengthening
from DSA) is suggested for future work.

Table 9.2 – Partial Chemical Compositions of the X70 Steel and a Theoretical Elevated Temperature
Alloy (ET-X70)

<table>
<thead>
<tr>
<th>wt pct</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>Nb</th>
<th>V</th>
<th>N</th>
<th>P</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>X70</td>
<td>0.045</td>
<td>1.57</td>
<td>0.30</td>
<td>0.29</td>
<td>0.25</td>
<td>0.094</td>
<td>0.015</td>
<td>0.065</td>
<td>0.005</td>
<td>0.005</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>ET-X70</td>
<td>0.045</td>
<td>1.57</td>
<td>0.30</td>
<td>0.10</td>
<td>0.50</td>
<td>0.50</td>
<td>0.02</td>
<td>0.065</td>
<td>0.10</td>
<td>0.005</td>
<td>0.010</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The second consideration regarding the design of the ET-X70 alloy was with respect to
weldability. X70 pipeline steels are typically hot rolled flat or coiled plate that is formed to the desired
pipe geometry and welded. Weldability was assessed in the X70 and ET-X70 steels with respect to
carbon, nickel, and chromium equivalencies (C_{eq} [142], N_{eq}, and Cr_{eq} [143] respectively) using

\[ C_{eq} = C + \frac{Mn}{6} + \frac{(Cr + Mo + V)}{5} + \frac{(Cu + Ni)}{15} \text{ (in wt pct)} \]  \hspace{1cm} (9.1)

\[ N_{eq} = Ni + 0.31Mn + 22C + 14.2N + Cu \text{ (in wt pct)} \]  \hspace{1cm} (9.2)

\[ Cr_{eq} = Cr + 1.37Mo + 1.5Si \text{ (in wt pct)} \]  \hspace{1cm} (9.3)

Figure 9.13 shows weldability diagrams based on comparing the carbon equivalent to the carbon
concentration and comparing the chromium and nickel equivalents to each other. The carbon, nickel, and
chromium equivalents were calculated for the X70 and ET-X70 steels and plotted on Figure 9.13. Both
steels were in Zone I in Figure 9.13a and the resistant zone in Figure 9.13b. It was determined that by first
inspection, both the X70 and ET-X70 steels were weldable.

The third consideration regarding the design on the ET-X70 alloy was the influence of the
alloying elements and processing conditions on the final microstructure. Ideally, the ET-X70
microstructure consists of quasi-polygonal ferrite, with austenite, MA constituent, and carbides present in
the ferrite grains, like the X70 steel studied in the present work. An equivalent microstructure between the
X70 and ET-X70 steels is desired so the influence of DSA and strain assisted bainitic tempering on the
mechanical properties can be assessed in the new alloy.
Figure 9.13  Weldability calculations of X70 and ET-X70 based on (a) the Graville diagram that compares the carbon concentration to the carbon equivalent to assess weldability based on cracking (figure re-drawn from Kurji and Coniglio [142]) and (b) a comparison of the chromium and nickel equivalents to assess weldability (figure adapted from Lippold [143]). Parameters for the X70 and ET-X70 steels were calculated using Equations 9.1-9.3 and plotted on the two weldability diagrams. (Color image, the reader is referred to the .pdf version of this document)

Changes in alloying elements could influence the final grain size, ferrite morphologies, hardenability, austenite stability, interstitial concentrations, and precipitate distributions in the ET-X70 steel. Further experimentation is suggested to assess the processing conditions required to achieve an ET-X70 microstructure equivalent to the X70 steel studied in the present work. Laboratory scale thermomechanical processing with a GLEEBLE® is recommended to study the microstructural evolution under different processing conditions. Figure 9.14 shows a schematic representation of the processing parameters used to make the X70 steel in the present study to achieve the as-received microstructure discussed above. The X70 steel was cast as an 85 mm slab and reheated to 1150 °C. One roughing pass at approximately 1100 °C (at approximately 45 pct reduction) and four finishing passes between 1050 and 880 °C were performed prior to coiling in the temperature range of 530 to 570 °C. Al-Jabr [114] discussed that lighter reductions were performed on the first two finish rolling steps and heavier
reductions were performed on the last finishing rolling steps in the production of the X70 steel in the
current study. However, the complete reduction schedules were not provided. The final thickness of the
X70 plate was 12.7 mm.

It was hypothesized that similar processing conditions can be used with the theoretical ET-X70
alloy to achieve the desired microstructure. However, the differences in alloying elements between the
X70 and ET-X70 steels cause differences in the $\text{Ac}_1$ and $\text{Ac}_3$ critical temperatures (i.e. the $\alpha+\text{Fe}_3\text{C}/\alpha+\gamma$
and $\alpha+\gamma/\gamma$ phase boundaries on heating respectively). Note, the critical temperatures during cooling ($\text{Ar}_3$
and $\text{Ar}_1$) are typically lower than the critical temperatures for heating. The theoretical critical
temperatures were calculated using the empirical relationships provided by Krauss [9]

$$\text{Ac}_3 = 910 - 203\sqrt{C} - 15.2N_i - 44.7S_i + 104V + 31.5Mo + 13.1W \quad 9.4$$

$$\text{Ac}_1 = 723 - 10.7Mn - 16.9Ni + 29.1Si + 16.9Cr + 290As + 6.38W \quad 9.5$$

where the concentrations of alloying elements are in wt pct. The calculated $\text{Ac}_3$ and $\text{Ac}_1$
temperatures were 879 and 714 °C respectively for the X70 steel and 905 and 722 °C respectively for the theoretical
ET-X70 steel. It is important to note that the hot roll finishing exit temperature (shown schematically
880 °C for the X70 steel was approximately equal to the $\text{Ac}_3$ temperature, which indicated that all hot
rolling was performed in the austenite phase field). Since the ET-X70 steel had a higher theoretical $\text{Ac}_3$
temperature compared to the X70 steel, the finishing exit temperature should be increased to
approximately 905 °C to enable hot rolling of austenite for all finishing passes (instead of the two-phase ferrite and austenite).

The finish rolling pass temperatures, finish pass reductions, coiling temperatures and cooling rates throughout the process can also be adjusted to achieve the target quasi-polygonal ferrite microstructure. After appropriate processing conditions have been established, elevated temperature tensile testing of an ET-X70 alloy (produced either as a laboratory or industrial trial heat) in the temperature range of 100-350 °C is suggested to assess the strengthening responses from DSA and strain assisted bainitic tempering.

1.41.2 A Note on Forming Operations within the DSA Regime

Interstitial-dislocation interactions during DSA are associated with many interesting material properties, such as increased strength, dislocation densities, and strain hardening rates. However, the DSA regime is typically avoided in metal forming operations because of surface flaws left by the deformation bands. The results in Chapter 4 discussed that the critical strain for serrated flow was greatest at the upper and lower boundaries of the DSA regime, and plastic deformation was uniform up to the critical strain. Also, the greatest amount of strengthening from DSA was observed at temperature/strain rate conditions near the upper bound of the DSA regime (associated with relatively high critical strains). If a forming process operating within the DSA regime wanted to avoid surface flaws from deformation bands and still obtain benefits from elevated temperature processing, the highest amount local deformation in the part could be designed to be less than the critical strain when operating near the upper boundary of the DSA regime. The result would be continuous yielding (i.e. no YPE), uniform deformation, and increased strengths from high strain hardening rates and dislocation densities.
CONCLUSIONS

The effects of deformation temperature near the dynamic strain aging (DSA) regime on the tensile properties of X70 and X52 line pipe steels were evaluated. Testing temperatures of interest were in the range of 25 to 350 °C, at engineering strain rates in the range of approximately $10^{-4}$ to $10^{-3}$ s$^{-1}$. The X70 steel had a quasi-polygonal ferrite microstructure with austenite, martensite-austenite, and carbide microconstituents present. The X52 steel was a control material (that exhibited elevated temperature behaviors comparable to observations in the DSA literature) that had a ferrite-pearlite microstructure.

Digital image correlation was used to characterize localized deformation associated with dynamic strain aging in X70 and X52 pipeline steels. Systematic changes in the localized deformation behaviors were observed by varying deformation temperatures and strain rates within the dynamic strain aging regime. Deformation band propagation and nucleation behaviors were directly related to the serration morphologies of the flow curves. It was concluded that relatively low and high frequency load drops in the flow curves were associated with deformation band propagation and nucleation respectively. A classification system was successfully developed to describe localized deformation behaviors associated with specific serration morphologies. Two types of deformation band propagation and two types of deformation band nucleation behaviors were observed in the pipeline steels when tested within the DSA regime between $10^{-3}$ and $10^{-4}$ s$^{-1}$. Discontinuous propagation (DP) was associated with unidirectional continuous movement of deformation bands along the gauge length (i.e. bands move in a single unique direction only) with nucleation events that occur when the deformation band front reaches one end of the gauge length. Continuous propagation (CP) was associated with the continuous movement of deformation bands along the gauge length and results in direction changes when the deformation front reaches the ends of the gauge length. Systematic nucleation (SN) was associated with quasi-random nucleation of deformation bands that occur anywhere along the gauge length at favorable sites based on the amount of local strain hardening at each potential nucleation site. Finally, constrained nucleation (CN) was associated with nucleation of bands where potential nucleation sites were constrained to occur adjacent to the previously deformed band and the overall behavior mimics either DP or CP characteristics.

Samples tested within the dynamic strain aging regime resulted in greater effective stress via interstitial atom-dislocation interactions which resulted in higher flow stress, greater dislocation densities, greater strain hardening rates, and reduced ductility compared to the room temperature conditions. Dynamic strain aging was also associated with negative strain rate sensitivities. The X70 steel exhibited dynamic strain aging over a slightly narrower temperature range than the X52 control material. However, both steels exhibited deformation band propagation and nucleation at relatively low and high temperatures within the dynamic strain aging regime respectively. At the upper and lower temperature
boundaries of the DSA regime, both steels exhibited relatively high critical strain CP deformation band behavior. Uniform deformation was observed prior to the critical strain.

Digital image correlation was also used with tests to determine strain rate sensitivities (i.e. m-values via the strain rate jump test) to assess the influence of dynamic strain aging on plastic instability. Negative strain rate sensitivities associated with samples tested within the DSA regime influenced necking behaviors in the pipeline steel tensile samples. Samples that exhibited negative jump test strain rate sensitivity m-values had (by qualitative comparisons) slightly more concentrated neck morphologies compared to samples with positive strain rate sensitivities. Necking initiated from previous CP or DP type deformation bands within the dynamic strain aging regime and concentrated at a slightly higher rate than samples that exhibited uniform plastic deformation.

It was also concluded that strain assisted bainitic tempering (i.e. tempering of the quasi-polygonal ferrite microstructure during plastic deformation) influenced the mechanical properties of the X70 steel at elevated temperatures just outside the dynamic strain aging regime. Decomposition of austenite grains in the microstructure and loss of the austenite transition carbide peaks in synchrotron wide-angle x-ray scattering were used as indicators of tempering of the quasi-polygonal ferrite microstructure. However, the volume fraction of austenite was relatively low and likely did not directly result in the property changes observed. Decomposition of austenite and transition carbides also resulted in higher concentrations of interstitial carbon atoms in ferrite (measured with internal friction) and caused the apparent activation volume (related to kink-pair configurations in the bcc lattice) to increase. Precipitation of cementite is also associated with the early stages of tempering and was hypothesized to be the primary source of the changes in elevated temperature mechanical properties observed outside the dynamic strain aging regime. At temperatures below 350 °C, bainitic tempering was highly strain dependent. However, bainitic tempering was observed prior to deformation when samples were heated to temperatures greater than approximately 350 °C. During tempering prior to deformation, precipitated cementite can coarsen and contribute less to the flow strength of the X70 steel.

Tensile testing under strain assisted bainitic tempering conditions resulted in increased flow strengths during uniform deformation (from the increased internal stress due to precipitation of fine cementite particles and relatively high dislocation densities), high strain hardening rates, and reduced ductility. Tempering is a diffusion based process that benefited from increased testing times associated with lower strain rates, which resulted in negative overall strain rate sensitivities. However, the instantaneous strain rate sensitivities (measured with the jump test method) were positive.

A theoretical X70 alloy designed for use at elevated temperatures was developed (referred to as ET-X70 in the text). The goal of the ET-X70 alloy was to achieve maximum elevated temperature strength by taking advantage of dynamic strain aging and strain assisted bainitic tempering. The ET-X70
alloy was designed to allow the precipitation of cementite particles during early stages of tempering of the quasi-polygonal ferrite structure but retard the coarsening (and thus softening) as much as possible with additions of carbide forming elements. The resulting fine cementite particles are theorized to provide greater flow stresses compared to the X70 steel studied in the present work.
FUTURE WORK

The elevated temperature mechanical properties of quasi-polygonal ferrite X70 pipeline steels were influenced by dynamic strain aging (DSA) and strain assisted bainitic tempering. The potential ideas for further experimental work on developing pipeline steels for use at elevated temperatures include: modeling interstitial-dislocation interactions during different regions within the DSA regime to develop a fundamental understanding of why the localized deformation band behaviors change, advanced characterization of the evolution of precipitates from strain assisted bainitic tempering, study the influence of traditional tempering at temperatures between 200-350 °C prior to elevated temperature deformation (i.e. an expansion of the low temperature aging study), systematic characterization of DSA and strain assisted bainitic tempering over a wide range of strain rates and temperatures, and development of the ET-X70 alloy discussed in Section 9.4.

Different types of behaviors related to deformation band propagation and nucleation were observed within the DSA regime. It was hypothesized that different interstitial-dislocation interaction models can be related to the type of deformation behaviors observed. For example, Leslie [13], modeled DSA as the permanent pinning of dislocations by solute atoms (making the pinned dislocations immobile), which results in the need for dislocation generation for deformation to continue. However, Schoeck and Seeger [81] discussed dynamic strain aging as the continuous pinning and un-pinning of dislocations during DSA. Internal friction theory suggests that the diffusivity of trapped interstitials is less than the diffusivity of free interstitials (i.e. the Snoek and SKK peaks occur at different temperatures and frequencies in the internal friction space). Future investigations could consider studies of the dislocation velocities (related to the plastic strain rate) in relation to the diffusion rates (related to the diffusivities) of trapped and free interstitials and apply the relationships in different areas of the DSA regime to various proposed DSA models from the literature. Further investigation relating the changes in the internal friction peaks during deformation within the DSA regime is also suggested. It is hypothesized that studying changes in the internal friction peak heights after straining at various conditions within the DSA regime could yield valuable information concerning interstitial-dislocation interactions.

Advanced characterization of precipitates in the X70 steel prior to straining and after deformation associated with strain assisted bainitic tempering is suggested as a continuation of the observations discussed in Chapter 9. Quantitative SEM, TEM, and synchrotron wide-, small-, and ultra-small-angle x-ray scattering (WAXS, SAXS, and U-SAXS) techniques are proposed to study the crystal structures, volume fractions, sizes, morphologies, and distributions of the various precipitates present in the X70 steels. Characterization of the precipitates during tensile deformation under strain assisted bainitic
tempering conditions will support the improvement of quasi-polygonal ferrite (and bainitic) steels for use at elevated temperatures.

The low temperature aging study from the MS thesis [12] and WAXS testing of the grip sections of samples tested at 350 °C indicated that bainitic tempering occurred when the X70 steels were exposed to elevated temperatures. An extensive study designed to investigate the influence of tempering at various temperatures and times on the elevated temperature mechanical properties of X70 steels is proposed. The results of such a study will provide insight on the stability of the bainitic microstructure at elevated temperatures, which will influence the suggested operating conditions for processes like steam assisted gravity drainage.

The strain rates studied in the present work spanned from $10^{-4}$ to $10^{-3}$ s$^{-1}$, which is a relatively narrow set of testing conditions. Therefore, a more extensive study on the elevated temperature mechanical properties of linepipe steels over a wider range of strain rates is proposed. Changing strain rates is hypothesized to influence the DSA and strain assisted bainitic tempering behaviors. At lower strain rates, more time is allowed for diffusion-based processes like precipitate coarsening or austenite decomposition. The DSA regime also shifts to lower temperatures at lower strain rates. At higher strain rates, the DSA regime shifts to higher temperatures and adiabatic heating can result in increased steel temperatures during deformation and thus faster tempering responses.

Finally, the development of the ET-X70 alloy introduced in Section 9.4 is proposed for future work. The ET-X70 alloy is designed to allow for the precipitation of cementite and retard cementite coarsening to stabilize the microstructure and provide as much precipitation strengthening during strain assisted bainitic tempering as possible. Processing conditions for optimal microstructures have yet to be established for the ET-X70 alloy. It is proposed that laboratory scale thermomechanical processing of an experimental ET-X70 heat be performed using a GLEEBLE® to assess the optimal processing conditions to achieve the desired quasi-polygonal ferrite microstructure. Prior to processing optimization, the elevated temperature mechanical properties of the ET-X70 alloy can be assessed with elevated temperature tensile testing and the results can be compared to the X70 alloy studied in the present work. Alternate alloying and processing strategies that have been used on commercial X70 steels are also suggested for investigation for developing optimized pipeline steels for used at elevated temperatures.
REFERENCES


[74] B. C. De Cooman, J. Kim, and S. Lee, “Heterogeneous Deformation in Twinning-Induced


APPENDIX A

SIMULATED d-SPACINGS

This appendix contains HEXRD® calculated d-spacings for diffraction analysis.

Table A.1 - Calculated d-Spacings for Ferrite, Austenite, and Cementite Peaks

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APPENDIX B

VIBRAN TORSIONAL PENDULUM USER MANUAL

This chapter was designed to give users a detailed list of procedures for running the Vibran torsional pendulum machine for measuring internal friction (See Figure 13.1). The torsional pendulum apparatus is capable of variable temperature (25 to at least 200 °C) and frequency (10^{-4} to 10 Hz) tests. There is a user manual made by Vibran for alignment and use of the machine. This user manual is helpful but not very descriptive. Use this document in parallel with the Vibran manual. Figure 13.1 shows the configuration of the machine while a test is running. The machine is suspended on a bungie system attached to a vibration dampening air table. The lab jack is used to support the machine while installing a sample or when the machine is not in use. Do not let the machine just hang freely when not running a test to keep the bungie system in good condition. The face shield is used to reduce air vibrations.

![Vibran Torsional Pendulum](image)

Figure B.1   Vibran torsional pendulum (fully assembled).

Internal friction is defined as the dissipation of mechanical energy connected with deviations from Hooke’s Law and, in steels, is a measure of anelastic (time dependent) diffusion/formation of free
interstitials (Snoek peak), trapped interstitials (Snoek-Ké-Koster or SKK peak), and dislocation kink formation (α and γ-Bordoni peaks). Other material defects (not discussed here) and phase transformations can contribute to internal friction, however such species are not commonly associated with steels. During an internal friction experiment, an elastic strain (usually on the order of $10^{-4}$) is applied and released continuously at a measurable temperature and loading frequency. Upon unloading, only a portion of the elastic strain is recovered instantaneously. The remainder of the elastic strain involves anelastic relaxation (also known as the elastic after-effect), which is a time dependent complete recovery from the initial strain.

A common sample geometry is shown in Figure 13.2. The machine is capable of handling samples with different gauge lengths (50 mm being the recommended maximum gauge length). The grip geometry and sample thickness should be held constant due to limitations in the torsional pendulum grips. Note: it may be possible to change the grip geometry slightly, as long as a 3.5 mm diameter hole is available for the screw clamps. SAMPLES MUST BE MACHINED USING EDM (see Waleed Al-Shalfan’s PhD thesis for a study on how different machining methods impact on results)!!!

![Internal friction specimen geometry](image)

Figure B.2 Internal friction specimen geometry. Dimensions are in mm. Machine using wire EDM only.

1.42 Alignment of the Torsional Pendulum

Alignment is extremely important to get good results for this technique. For a complete alignment procedure, read the Vibran user manual. It does a good job identifying what key alignment steps are necessary. This manual will focus on assuming certain components are already well aligned. Note, many of the parts of the full alignment procedure are redundant after being performed once. You do not need to do every step from sample to sample.

To start an experiment, start with the torsional pendulum in the configuration illustrated by Figure 13.3. Jack up the lab jack so that the apparatus is resting on the jack with no front plastic shield attached (i.e. the front of the machine is open). If a sample is in the machine, remove the sample by sliding the
furnace down to expose the sample. Set aside the top grip, 200 g weight, and sample. Follow the following Figures. Descriptions of each step are in the captions.

Figure B.3 Starting configuration to insert a new specimen. Face shield is removed, the lab jack is raised to support the machine. Sample and top grip are set aside.

Figure B.4 Insert top grip through hole on top of the machine. Thread string through pulleys and attach weight for stability.
Figure B.5  Lift the magnetic furnace and loosen the lower grip fix screw with the wrench. The lower grip should be able to rotate freely now. Lower the furnace again.

Figure B.6  Attach sample to top grip and insert the flat-head screw. Do not tighten screw down just yet. Sample should be able to rotate slightly in the top grip. Position the top grip so the permanent magnet is centered vertically in the viewing port. Rotate the bottom grip (to adjust lower grip height) so the sample can be clamped into the bottom grip where the whole assembly allows the permanent magnet to be vertically centered in the electro-magnet. The mirror on the top grip must be facing the laser, therefore you must adjust the bottom grip in half turns only. Attach sample to bottom grip. Do no tighten flat-head screw yet. The sample should be able to rotate and tilt in the internal friction machine now.
Figure B.7 If you have a magnetic sample, attach bubble level to sample and lower the lab jack so the machine hangs freely. Add weights to the machine so the whole system hangs level (use 2D bubble level to verify this). Adjust the sample so the bubble level reads level (Figure 13.7b). Then tighten the flat-head screws to finger tight. Raise the jab jack to support the torsional pendulum again. Remove the bubble level.

Figure B.8 Rotate bottom grip slightly so that the permanent magnet is rotationally aligned in the electro-magnet. A good method to do this is to use a cell phone camera placed on top of the machine looking down the torsional axis. The permanent magnet can be viewed on the cell phone. Rotate the bottom grip until the flat surface of the permanent magnet is parallel to the electro-magnet hole flat surface. While maintaining this alignment tighten the lower grip fix screw with your fingers. The assemble should now be both vertically and rotationally centered in the electromagnet.
Figure B.9   Raise the furnace over the sample and fix it to the bottom grip using the insulation fixture. Do not over-tighten the bolts in the insulation (they will strip easily). Make sure the furnace is aligned parallel to the sample.

Figure B.10   Turn on the FLDMA-2001 controller (powers everything but the furnace) and the computer. The laser should be on now. Use the rotation adjustment so adjust the laser so it hits the center of the mirror on the top grip. Once centered on the sample tighten the set screw to finger tight to lock the laser rotation position. Look through the felt hole and adjust the laser focus to make the red dot as fine as possible. Adjust the laser height so that the laser beam is vertically centered on the light sensor. Slightly adjust the lower grip with the wrench until the laser is touching the sensor Laser may not hit center of sensor yet. (If laser cannot hit sensor you may need to manually adjust the position of the Newport Motor using either the Vibran or Newport Controller SEE LATER IN THIS MANUAL IF YOU NEED TO USE THE NEWPORT CONTROLLER!!!  **DO NOT** UNPLUG THE NEWPORT MOTOR WHILE POWER IS ON!!!!!!!!!!!!)
Open Interstitial Analyzer IA-202 on the computer. Click the “Zero” on the top menu to open the zero-position measurement window. Click the “Measure” button. In this step, you are moving the sensor into the path of the laser. If the sensor is only slightly off from the laser point you can use the manual zero control arrows to move the sensor so the laser is reading a voltage less than 5V (note voltage can be negative so use the absolute value). Be careful because the manual zero control can attempt to move the Newport motor too far which can damage the motor so pay attention to the current position of the motor). Adjust the bottom grip rotation slightly if the motor will move too far to the right. Once you are reading a voltage and you have verified that the motor will not move too far to hit the end of travel to get the laser to the center of the sensor, enable automatic zero control (check box) and click the “Execute” button. The motor will automatically move the sensor so that the laser hits the center. The readout should read less than 0.001V if the sensor is properly centered. This value may want to drift so you may need to hit the “Execute” button again a few times until the voltage value is stable. Note the lab jack is still up and supporting the torsional pendulum. You will need to repeat the zero step again later when the system is hanging freely. It is important to run this step first because there may need to be adjustments to the system and you do not want to be raising and lowering the system over and over. When you are satisfied with the zero position, click “Stop” and “Exit.”

If this step is not possible, see later in this manual (in the Newport Controller Section) to use the Newport controller to move the sensor closer to where you need it to be. **DO NOT UNPLUG THE NEWPORT MOTOR WHILE POWER IS ON!!!!!!!!!!!**
Figure B.12 At this point be prepared to restart the computer often! After you run a Free Decay Vibrating Test and realize adjustments to the alignment are needed restart the computer! The restart does not take long and it will remove many bugs/glitches that you might run into otherwise. Restart from Figure 13.11 after each computer restart.

Click the “Decay” button to open the Free Decay Vibrating Test. This test is used to determine if your alignment is appropriate for an internal friction experiment. If you are using steel type in the indicated detection parameters (if you are not using steel try to get close to your parameters and you must be close (order of magnitude for your $Q^{-1}$) to get this step to work properly). Click the “Measure” button. You will see the displacement percentage increase. This value must start at about 0% and reach 100% or the software will crash (if this happens restart the computer, perform zero position measurement in Figure 13.11 and run free decay again) or your alignment is probably off. After the calculation is complete the program will give you a plot of the vibration data, the vibration frequency of the sample, the internal friction ($Q^{-1}$) measured, and a quality coefficient. The quality coefficient is a measure of your system alignment with a range of 0-1 and must be >0.999. Try running this measurement more than once if you achieve a quality coefficient >0.9, the value might get better.

If you achieve a good quality coefficient, click “Exit,” restart the computer, put the front face shield on the system and lower the lab jack. Repeat the Zero Position Measurement and Free Decay Vibrating Test again. You should be able to achieve a greater quality coefficient value than before.

If you are having a hard time getting a good quality coefficient, your alignment is off somewhere or your guessed values for frequency and $Q^{-1}$ is too far off. Try rotating the sample in the bottom grip slightly, moving the bottom grip up or down by ½ rotation, changing the position of the furnace, make sure the laser is hitting the center of the mirror and is centered vertically on the light sensor. The output graph can help. If the sine waves are not centered about zero, the laser is not oscillating about the center of the light sensor and your zero position is probably off. If there is a beat to your data (i.e. irregular amplitudes in the decaying plot) your permanent magnet is probably not centered properly in the electro-magnet (rotationally or vertically). If the sample decays too fast to a zero point your guessed values are probably off.
1.43 Running an Internal Friction Experiment

Once the torsional pendulum has the front face shield in place, is hanging freely, and has achieved a good quality coefficient you can move on to running an internal friction experiment.

Figure B.13 Click the “Forced” button to open the Forced Vibration Test window. This test is used to calibrate the voltage needed to achieve the correct amount of strain during the vibrations for internal friction measurements. The light sensor measures position as a voltage. 0.000 V indicates the center of the sensor and ±5.000 V indicates the ends of the sensor. The machine is designed to measure internal friction when vibrating between ±4 V (3.9 V < amplitude < 4.1 V required) to ensure the laser never leaves the light sensor during vibrations. Use a frequency of 10 Hz and select High precision and Pendulum mode. Click the “Measure” button. You can watch the laser oscillate on the sensor for this part. The machine guessed an applied voltage and outputted the amplitude (which for the first measurement is never correct and is usually less than the required 4.0 V). Click the “Measure” button again and the final amplitude should be within the required range.
Go to Parameter → Set Parameter to open the Experimental Parameter Set window. This window lets you program your internal friction test and is the last step you need to perform before running an experiment. There are four areas of control: Temperature, Time, Frequency, and Temperature Control.

Temperature is for controlling the sample temperature with the magnetic furnace (note if you want to do temperature control you must turn on the temperature controller located above the LFDMA-2001 controller, and turn the knobs past clockwise past their zero point to give the furnace power). Set the temperature range and jump interval here. For a room temperature test use the indicated values.

Time holds parameters for the time at temperature. I have not played with this very much and might update this part in a later version of the user manual.

Frequency parameters are for the maximum and minimum frequencies during the test and the number of data points you want in your data set. 41 data points is a good number for a room temperature-variable frequency experiment.

Temperature Control parameters control the heating rate, control thermocouples (1 is the furnace thermocouple and 2 is the sample thermocouple).

Once you have defined the parameters you want for your internal friction test click the OK button and then Click the “Transfer” button in the top menu. If you use the indicated parameters for a room temperature-variable frequency experiment you can get about 11 cycles of data (i.e. 11 data points per frequency condition) in 24 h.
To perform a room temperature-variable frequency test select the “Measure-Time” button. This will run your parameters with only vibration control (i.e. there is no temperature control and you do not need the temperature controller to be turned on). Click the “Measure” button to start the test. Your data will display on the figure in real time. The Exciting Frequency indicates the frequency currently being measured, and the Measuring percentage indicates the progress for each measurement. The data is automatically being written to a .dat file indicated at the top of the screen (note: the number assigned here indicates the date of the experiment, but since this computer was made before the year 2000 the date function does not work since the computer does not know what to do past the year 2000, so you will need to rename your files later). The directory where your data is being stored is indicated at the top of the screen as well. I suggest immediately copying your newly generated data at the end of the test to a floppy disk and use the floppy to USB converter to get your data between experiments. That way you are not relying on the old computer to store your data.

While running a test the machine will start at the high frequencies and move to the low frequencies. Once the last data point is measured at the lowest frequency, the machine will start the analysis again automatically. This is nice because you can let the machine sit for several hours/days and get multiple data points per condition.
APPENDIX C

SERRATION MORPHOLOGY STUDY

The following figures are load-time curves from the serration morphology study used to fully define the lower temperature deformation band behaviors within the DSA regime. Additional morphologies were presented in the MS work [12] and in Chapter 4. Classifications of the deformation behavior are the authors best estimation based on comparisons of the flow curve morphologies discussed in Chapter 4.

![Figure C.1 Load-time curves from the serration morphology study.](image)
Figure C.2 Load-time curves from the serration morphology study.
Figure C.3  Load-time curves from the serration morphology study.
Figure C.4 Load-time curves from the serration morphology study.
APPENDIX D

STRESS RELAXATION ANALYSIS PARAMETERS

This appendix includes tables of all the parameters used to fit the stress relaxation data using the activation volume and internal/effective stress models, where $T$ is the temperature, $e$ is the engineering strain of the hold, $\sigma$ is the (true) flow stress, $V_{\text{app/b}^3}$ is the normalized apparent activation volume, $C_r$ is the time constant parameter used in the activation volume analysis, $m^*$ is the dislocation velocity-stress exponent, $a$ is the integration constant parameter that was assumed to be 0.5, $\sigma_i$ is the internal stress, and $\sigma^*$ is the effective stress.

Table D.1 - Fitting Parameters for Stress Relaxation Testing

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<th>Steel</th>
<th>$T$ (°C)</th>
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<th>$\sigma$ (MPa)</th>
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### Table D.1 - Fitting Parameters for Stress Relaxation Testing (continued)

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APPENDIX E

X-RAY DIFFRACTION MEASURED PEAK INTENSITIES

This appendix includes supplementary information regarding WAXS measurements in the pipeline steels discussed in Chapter 6. The tables that follow are measured peak intensities from APS and CHESS line scans.

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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.719</td>
<td>0.0062</td>
<td>0.0065</td>
<td>0.0098</td>
<td>0.0053</td>
<td>0.0073</td>
<td>0.0045</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Values in parenthesis indicate that the observed peak was very close to background intensity.
Table E.2 - Normalized Intensities of X70 Peaks Observed in the CHESS Results

<table>
<thead>
<tr>
<th>20 (°)</th>
<th>d (Å)</th>
<th>Near BKG Intensity? (Y/N)</th>
<th>X70 Normalized Intensity at 61.332 keV (1 mm thick internal friction samples, engineering strains were approximately equal to 5 pct, strain rate = (10^4) s(^{-1}))</th>
<th>Estimated Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>AR</td>
<td>300°C_G</td>
</tr>
<tr>
<td>5.563</td>
<td>2.083</td>
<td>N(Y)</td>
<td>0.0091</td>
<td>0.0091</td>
</tr>
<tr>
<td>5.706</td>
<td>2.030</td>
<td>N</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6.196</td>
<td>1.870</td>
<td>Y</td>
<td>0.0016</td>
<td>0.0019</td>
</tr>
<tr>
<td>6.412</td>
<td>1.807</td>
<td>N(Y)</td>
<td>0.0036</td>
<td>0.0046</td>
</tr>
<tr>
<td>8.071</td>
<td>1.438</td>
<td>N</td>
<td>0.0124</td>
<td>0.0449</td>
</tr>
<tr>
<td>9.097</td>
<td>1.275</td>
<td>N(Y)</td>
<td>0.0010</td>
<td>0.0018</td>
</tr>
<tr>
<td>9.505</td>
<td>1.222</td>
<td>Y</td>
<td>0.0011</td>
<td>-</td>
</tr>
<tr>
<td>9.890</td>
<td>1.174</td>
<td>N</td>
<td>0.0758</td>
<td>0.1085</td>
</tr>
<tr>
<td>10.266</td>
<td>1.133</td>
<td>Y</td>
<td>0.0012</td>
<td>0.0015</td>
</tr>
<tr>
<td>11.116</td>
<td>1.044</td>
<td>N(Y)</td>
<td>0.0016</td>
<td>0.0019</td>
</tr>
<tr>
<td>11.421</td>
<td>1.017</td>
<td>N</td>
<td>0.0534</td>
<td>0.0564</td>
</tr>
<tr>
<td>12.759</td>
<td>0.910</td>
<td>N</td>
<td>0.0240</td>
<td>0.0405</td>
</tr>
</tbody>
</table>

* Indicates a peak that was observed near the edge of one of the six x-ray detectors and was not detected in the line scan integration.
** WAXS scans 300 °C_G and 350 °C_G were taken from grip sections of internal friction bars (strain = 0 pct).

Table E.3 - Normalized Intensities of X52 Peaks Observed in the CHESS Results

<table>
<thead>
<tr>
<th>20 (°)</th>
<th>d (Å)</th>
<th>Near BKG Intensity? (Y/N)</th>
<th>X52 Normalized Intensity at 61.332 keV (1 mm thick internal friction samples, engineering strains were approximately equal 5 pct, strain rate = (10^4) s(^{-1}))</th>
<th>Estimated Index or Other</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>AR</td>
<td>25 °C</td>
</tr>
<tr>
<td>5.434</td>
<td>2.132</td>
<td>Y</td>
<td>0.0027</td>
<td>-</td>
</tr>
<tr>
<td>5.706</td>
<td>2.030</td>
<td>N</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6.196</td>
<td>1.870</td>
<td>N(Y)</td>
<td>0.0020</td>
<td>(0.0018)</td>
</tr>
<tr>
<td>8.071</td>
<td>1.438</td>
<td>N</td>
<td>0.0788</td>
<td>0.0316</td>
</tr>
<tr>
<td>9.890</td>
<td>1.174</td>
<td>N</td>
<td>0.0934</td>
<td>0.0724</td>
</tr>
<tr>
<td>11.421</td>
<td>1.017</td>
<td>N</td>
<td>0.0613</td>
<td>0.0521</td>
</tr>
<tr>
<td>12.759</td>
<td>0.910</td>
<td>N</td>
<td>0.0400</td>
<td>0.0301</td>
</tr>
</tbody>
</table>
Table E.4 - Normalized Intensities of X70 Peaks Observed in the CHESS Results

<table>
<thead>
<tr>
<th>20 (°)</th>
<th>d (Å)</th>
<th>Near BKG Intensity?</th>
<th>X70 Normalized Intensity at 61.332 keV (approximately 1 mm thick internal tensile samples, engineering strains measured with DIC, strain rate = 10^4 s^-1)</th>
<th>Estimated Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 °C (9.0 pct)</td>
<td>150 °C (6.5 pct)</td>
</tr>
<tr>
<td>5.563</td>
<td>2.083</td>
<td>N/(Y)</td>
<td>(0.0187)</td>
<td>0.0159</td>
</tr>
<tr>
<td>5.706</td>
<td>2.030</td>
<td>N</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6.196</td>
<td>1.870</td>
<td>Y</td>
<td>0.0108</td>
<td>-</td>
</tr>
<tr>
<td>6.412</td>
<td>1.807</td>
<td>N/(Y)</td>
<td>(0.0109)</td>
<td>0.0100</td>
</tr>
<tr>
<td>8.071</td>
<td>1.438</td>
<td>N</td>
<td>0.4032</td>
<td>0.3891</td>
</tr>
<tr>
<td>9.097</td>
<td>1.275</td>
<td>N/(Y)</td>
<td>(0.0116)</td>
<td>0.0106</td>
</tr>
<tr>
<td>9.890</td>
<td>1.174</td>
<td>N</td>
<td>0.6443</td>
<td>0.4780</td>
</tr>
<tr>
<td>*</td>
<td>*</td>
<td>N/(Y)</td>
<td>(*)</td>
<td>*</td>
</tr>
<tr>
<td>11.116</td>
<td>1.044</td>
<td>N/(Y)</td>
<td>(0.0101)</td>
<td>0.0051</td>
</tr>
<tr>
<td>11.421</td>
<td>1.017</td>
<td>N</td>
<td>0.1081</td>
<td>0.0567</td>
</tr>
<tr>
<td>12.759</td>
<td>0.910</td>
<td>N</td>
<td>0.0439</td>
<td>0.1586</td>
</tr>
</tbody>
</table>

* Indicates a peak that was observed near the edge of one of the six x-ray detectors and was not detected in the line scan integration.

Table E.5 - Normalized Intensities of X52 Peaks Observed in the CHESS Results

<table>
<thead>
<tr>
<th>20 (°)</th>
<th>d (Å)</th>
<th>Near BKG Intensity?</th>
<th>X52 Normalized Intensity at 61.332 keV (approximately 1 mm thick internal tensile samples, engineering strains measured with DIC, strain rate = 10^4 s^-1)</th>
<th>Estimated Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 °C (18.6 pct)</td>
<td>201 °C (14.1 pct)</td>
</tr>
<tr>
<td>5.706</td>
<td>2.030</td>
<td>N</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6.196</td>
<td>1.870</td>
<td>Y</td>
<td>0.0035</td>
<td>0.0032</td>
</tr>
<tr>
<td>8.071</td>
<td>1.438</td>
<td>N</td>
<td>0.2125</td>
<td>0.1434</td>
</tr>
<tr>
<td>9.890</td>
<td>1.174</td>
<td>N</td>
<td>0.3480</td>
<td>0.2590</td>
</tr>
<tr>
<td>11.421</td>
<td>1.017</td>
<td>N</td>
<td>0.0530</td>
<td>0.0606</td>
</tr>
<tr>
<td>12.759</td>
<td>0.910</td>
<td>N</td>
<td>0.0764</td>
<td>0.0818</td>
</tr>
</tbody>
</table>
APPENDIX F

INTERNAL FRICTION DEBYE FIT PARAMETERS

This appendix includes the Debye and background fitting parameters from the torsional pendulum internal friction analysis. Table 17.1 shows the measured parameters from the internal friction analysis. The data shown in Table 17.1 was presented in Chapter 8 and was incorporated in the discussions in Chapter 9. For reference, the multiple Debye peak fitting equation used was

\[ Q^{-1} = y_0 + C e^{(-d(2\pi f))} + \sum_i \frac{2Q_{\text{Max}(i)}^{-1} T_0, i e^{(Q_i/kT)} (2\pi f)}{1 + (2\pi f)^2 \left[\tau_0, i e^{(Q_i/kT)}\right]^2} \]

where \( y_0 \), \( C \), and \( d \) are background fitting parameters and \( Q_{\text{Max}(i)}^{-1} \) is the Debye peak height of either the C-Snoek or \( \gamma \)-Bordoni peaks. See Table 2.2 (Section 2.6) for the activation energy \( (Q_i) \) and mean residence time \( (\tau_{0,i}) \) constants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>n</th>
<th>( y_0 )</th>
<th>C</th>
<th>d</th>
<th>( Q_{\text{Max}(C)}^{-1} )</th>
<th>( Q_{\text{Max}(\gamma)}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X70_10</td>
<td>AR</td>
<td>12</td>
<td>5.85E-05</td>
<td>4.25E-05</td>
<td>0.09139</td>
<td>7.49E-05</td>
<td>1.26E-04</td>
</tr>
<tr>
<td>X70_10</td>
<td>25 °C 3 pct</td>
<td>3</td>
<td>2.39E-04</td>
<td>1.28E-04</td>
<td>0.17721</td>
<td>2.03E-05</td>
<td>1.32E-04</td>
</tr>
<tr>
<td>X70_21</td>
<td>AR</td>
<td>11</td>
<td>2.09E-04</td>
<td>8.26E-05</td>
<td>0.28649</td>
<td>5.21E-05</td>
<td>1.28E-04</td>
</tr>
<tr>
<td>X70_21</td>
<td>150 °C 3 pct</td>
<td>10</td>
<td>1.95E-04</td>
<td>1.58E-04</td>
<td>0.14975</td>
<td>2.00E-05</td>
<td>1.51E-04</td>
</tr>
<tr>
<td>X70_20</td>
<td>AR</td>
<td>11</td>
<td>8.60E-05</td>
<td>5.98E-05</td>
<td>0.14614</td>
<td>7.12E-05</td>
<td>1.41E-04</td>
</tr>
<tr>
<td>X70_20</td>
<td>212 °C 3 pct</td>
<td>10</td>
<td>9.03E-05</td>
<td>9.69E-05</td>
<td>0.23679</td>
<td>4.81E-05</td>
<td>1.26E-04</td>
</tr>
<tr>
<td>X70_18</td>
<td>AR</td>
<td>22</td>
<td>9.52E-05</td>
<td>6.09E-05</td>
<td>0.23046</td>
<td>7.54E-05</td>
<td>1.19E-04</td>
</tr>
<tr>
<td>X70_18</td>
<td>314 °C 3 pct</td>
<td>11</td>
<td>7.31E-05</td>
<td>3.95E-05</td>
<td>0.20363</td>
<td>7.49E-05</td>
<td>1.19E-04</td>
</tr>
<tr>
<td>X70_23</td>
<td>AR</td>
<td>11</td>
<td>1.09E-04</td>
<td>4.48E-05</td>
<td>0.14955</td>
<td>5.45E-05</td>
<td>1.04E-04</td>
</tr>
<tr>
<td>X70_23</td>
<td>25 °C 3 pct</td>
<td>5</td>
<td>2.37E-04</td>
<td>1.48E-04</td>
<td>1.67E-01</td>
<td>1.07E-05</td>
<td>1.15E-04</td>
</tr>
<tr>
<td>X52_18</td>
<td>AR</td>
<td>10</td>
<td>2.29E-04</td>
<td>3.60E-05</td>
<td>0.03075</td>
<td>1.12E-04</td>
<td>1.11E-04</td>
</tr>
<tr>
<td>X52_18</td>
<td>25 °C 3 pct</td>
<td>18</td>
<td>2.63E-04</td>
<td>1.19E-04</td>
<td>0.20735</td>
<td>4.39E-05</td>
<td>5.58E-05</td>
</tr>
<tr>
<td>X52_20</td>
<td>AR</td>
<td>10</td>
<td>2.79E-04</td>
<td>1.10E-04</td>
<td>0.18857</td>
<td>5.15E-05</td>
<td>6.20E-05</td>
</tr>
<tr>
<td>X52_20</td>
<td>25 °C 3 pct</td>
<td>13</td>
<td>2.20E-04</td>
<td>2.99E-05</td>
<td>0.05523</td>
<td>9.90E-05</td>
<td>1.06E-04</td>
</tr>
<tr>
<td>X52_15</td>
<td>AR</td>
<td>10</td>
<td>2.83E-04</td>
<td>5.80E-05</td>
<td>0.10144</td>
<td>1.09E-04</td>
<td>1.35E-04</td>
</tr>
<tr>
<td>X52_15</td>
<td>129 °C 3 pct</td>
<td>8</td>
<td>2.72E-04</td>
<td>1.36E-04</td>
<td>0.19023</td>
<td>4.30E-05</td>
<td>8.31E-05</td>
</tr>
<tr>
<td>X52_16</td>
<td>AR</td>
<td>7</td>
<td>2.00E-04</td>
<td>7.66E-05</td>
<td>1.08E-02</td>
<td>1.35E-04</td>
<td>1.63E-04</td>
</tr>
<tr>
<td>X52_16</td>
<td>208 °C 3 pct</td>
<td>12</td>
<td>1.70E-04</td>
<td>8.50E-05</td>
<td>0.19471</td>
<td>6.19E-05</td>
<td>1.27E-04</td>
</tr>
<tr>
<td>X52_17</td>
<td>AR</td>
<td>11</td>
<td>2.39E-04</td>
<td>4.64E-05</td>
<td>0.05246</td>
<td>1.19E-04</td>
<td>1.39E-04</td>
</tr>
<tr>
<td>X52_17</td>
<td>300 °C 3 pct</td>
<td>11</td>
<td>1.50E-04</td>
<td>5.67E-05</td>
<td>0.19256</td>
<td>8.25E-05</td>
<td>1.16E-04</td>
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</tbody>
</table>