Improved Resistance to Hydrogen-Induced Cracking by Tempering of Intercritically Rolled Accelerated-Cooled X65 Steel



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Hydrogen-induced cracking (HIC) occurs in pipeline steels used in oil and gas applications that are rich in hydrogen sulfide gas also known as sour service environments. In this study, an experimental X65 steel was produced by intercritically finish rolling, accelerated cooling, then air-cooling to room temperature. This thermo-mechanical processing scheme resulted in a mixture of quasi-polygonal ferrite and martensite/austenite (M/A) microconstituents, also known as granular bainite. Sections from the steel were also tempered at 300 °C, 400 °C, 500 °C, and 600 °C for 40 min, which resulted in a significant increase in HIC resistance and impact toughness, along with a marginal increase in yield strength and maintenance of untempered hardness. The evolution of HIC resistance, tensile properties, and impact toughness is discussed in the context of phase fraction, dislocation density, and microstructural evolution. The current work demonstrates the potential for tempering after thermo-mechanical processing to reduce HIC susceptibility and increase impact toughness while nominally maintaining yield strength and hardness in microalloyed pipeline steels.

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I. INTRODUCTION

HYDROGEN-INDUCED cracking is a phenomenon that occurs in oil and gas applications that contain high partial pressures of hydrogen sulfide (H₂S) gas, also known as sour service. The presence of sulfur in H₂S gas acts as a hydrogen recombination inhibitor that subsequently increases ingress of hydrogen ions into the steel. It is currently believed that the accumulation and recombination of hydrogen ions into H₂ molecules at sites in the steel with high hydrogen trapping energy, such as inclusions or interphase boundaries, can initiate internal voids that grow into cracks by internal pressurization. Current industrial practice requires a maximum yield strength of 800 MPa (116 ksi) for steels destined for sour service per NACE MR0175/ISO 15156.^[1] This industrial practice is informed by the

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oft-cited belief in literature that HIC susceptibility increases with strength. In fully martensitic, medium carbon steels, tempering is a well-established mechanism of reducing hydrogen embrittlement (HE) susceptibility for high strength fastener applications.^[2] Improvement in HE susceptibility upon tempering in fully martensitic steel is usually attributed to the observed reduction in strength.

As far as the authors are aware, no studies of the effect of tempering on thermo-mechanically processed (TMP), accelerated-cooled line pipe steels exist at the time of publication. One study of the effect of tempering of a granular bainitic offshore platform steel was conducted by Zhou *et al.*^[3] The steel has similar alloy content to the steel in the current study except for 1.18 wt pct Ni, and a similar TMP treatment apart from accelerated cooling initiating in the single-phase austenite regime. The study utilized tempering treatments for 60 min at 300 °C, 400 °C, 500 °C, and 600 °C, which resulted in improved toughness and a reduced tensile strength that the authors attributed to the decomposition of M/A. The study did not measure the phase fraction evolution upon tempering. However, the evolution of fully martensitic microstructures upon tempering is well characterized and is used here as a groundwork for understanding the evolution of martensite/austenite (M/A) constituents during tempering. The

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stages of tempering in martensitic steel occur over four temperature regimes.^[3,4] Stage I of tempering occurs at temperatures up to 200 °C. At temperatures less than 100 °C coherent η carbides form, while at temperatures between 100 and 200 °C, ε carbides (Fe_{2.4}C) form. The formation of these carbides is dependent on alloy composition, most importantly carbon content.^[5] Stage II of tempering involves the decomposition of austenite to ferrite and cementite or χ Haag carbides (Fe₅C₂), and occurs from 200 to 300 °C. Stage III occurs over a wide range of temperatures above 300 °C, involves the decomposition of austenite, and leads to the formation of ferrite and cementite by the dissolution of previously formed transition carbides. Recovery can take place above 400 °C, and recrystallization can take place between 600 and 700 °C. Lastly, secondary hardening from precipitation of alloy carbides occurs during stage IV of tempering from 500 to 600 °C, particularly in molybdenum (Mo), vanadium (V), and titanium (Ti) containing steels. The exact temperatures associated with the four stages of tempering in martensitic steels can vary with alloy content.

The strengthening mechanisms inherent to martensite (i.e., high dislocation density, carbon solid solution strengthening, precipitation strengthening, and grain size strengthening) are affected by tempering. In martensitic steels, hardness generally decreases with increasing tempering time and temperature.^[5] Additionally, Charpy impact toughness is known to increase with tempering temperature in fully martensitic microstructures, except in the temper embrittlement and tempered martensite embrittlement regimes.^[4,6-9] However, the tempering response of fully bainitic microstructures, which are more relevant to the microstructure of this study, has additional complexities to consider. Tempering of martensite involves the diffusion of carbon atoms from the supersaturated matrix to form carbides. The slower cooling rates required for bainite formation allow for carbon diffusion and precipitation of cementite. Because the amount of solute carbon is lower in bainitic microstructures in the as-received condition, hardness does not decrease significantly at low tempering temperatures in bainitic microstructures.^[10–12] Further complicating tempering effects, the granular bainitic microstructure relevant to accelerated-cooled pipeline steels consists of multiple constituents including bainitic ferrite and small islands of M/A.^[13,14] These microconstituents likely have a different tempering response, though the most significant differences are likely in M/ A. Because M/A constituents are frequently associated with HIC in literature,^[15–18] this study seeks to investigate the relationship between tempering of granular bainite, in particular M/A constituents, and HIC resistance, impact toughness, and tensile strength.

II. EXPERIMENTAL

A custom X65 steel ingot was cast in a 12.7 cm (5 in) \times 12.7 cm (5 in) \times 25.4 cm (10 in) billet with the chemistry shown in Table I, and subsequently underwent thermo-mechanical processing (TMP) as shown

 Table I.
 Chemical Composition of X65 Plate Steel (Weight Percent)

С	Mn	Si	Ni	Cr	Ti	Mo	Nb
0.0433	1.229	0.271	0.156	0.291	0.020	_	0.049
V	Al	Ν	S		Р	Cu	Ca
0.033	0.037	0.0053	0.00	01 0	0.011	_	0.0009

schematically in Figure 1. Casting and thermos-mechanical processing of the steel was conducted by Arcelor Mittal. Rough rolling was conducted above the temperature for no-recrystallization (T_{NR}), which was calculated to be ≈ 1004 °C based on the Boratto et al. equation.^[19] The alloy was finish rolled between 950 and 775 °C, accelerated-cooled down to 590 °C, and then air-cooled. The steel was finish rolled in the intercritical regime to increase the dislocation density imparted in the ferrite. The intercritical finish rolling and subsequent increased dislocation density was desirable in the context of a separate study on the effect of finish rolling temperature on HIC.^[20] In order to determine an intercritical finish rolling temperature for processing, the ferrite start and finish temperatures, A_{r1} and A_{r3}, were determined using dilatometry on the as-cast material.^[20]

Four blanks (dimensions in Figure 2) of the accelerated-cooled X65 steel were tempered for 40 min at 300, 400, 500, and 600 °C using box furnaces with thermal masses. The temperature of the specimen blocks was recorded and monitored using a thermocouple in contact with the top of the blank, and the 40-min timer initiated when the top surface of the blanks was within 5 °C of the desired temperature. After tempering for 40 min, the blanks were removed from the furnace and air-cooled.

Samples for tensile testing and impact testing were machined from the blanks as shown in Figures 2(a)through (c). The tensile specimens were oriented with the tensile axis parallel to the transverse direction (TD) of the plate. The Charpy specimens were machined with the notch parallel to the normal direction-rolling direction (ND-RD) plane. Two sub-size E8 tensile specimens (Figure 2(b)) and six Charpy specimens (Figure 2(c)) were obtained from each heat-treated section.^[21,22] Uniaxial tensile tests were conducted at room temperature (21 °C \pm 1 °C) using a 90 kN (20,000 lb) capacity Instru-Met screw driven electromechanical tensile frame. The tests were performed with a 0.0127 mm \min^{-1} (0.0005 in \min^{-1}) crosshead speed and a data acquisition rate of 20 Hz. Displacement was measured using a 2.54 cm (1-in.) Shepic extensometer. Charpy tests were conducted at the National Institute for Standards and Technology in Boulder, CO on a large capacity machine (950 J potential energy). Three Charpy tests per heat treatment condition were conducted at room temperature to determine the room temperature (21 \pm 1 °C) absorbed energy, and three additional samples were used for testing at low temperatures. Additionally, Vickers hardness tests were



Fig. 1—Schematic demonstrating the thermomechanical processing path of the X65 steel, which was finish rolled from 950 to 775 $^{\circ}$ C, accelerated-cooled down to 590 $^{\circ}$ C and then air-cooled. Reprinted from—Ref. 20.

conducted using a 500 g load with a 10 s dwell time, utilizing five indents per sample condition.

Specimens for HIC testing were machined from the plate to a final dimension of 20 ± 1 mm in the transverse direction, and 100 ± 1 mm in the rolling direction, shown schematically in Figure 3(a). The samples retained the full as-received thickness in the normal direction, which was approximately 12.5 mm. Three samples with these dimensions were machined from blocks of each condition, as shown in Figure 3(a). NACE TM0284 testing^[23] was conducted by Evraz North America at their Research and Development facilities located in Regina, Saskatchewan. The NACE TM0284 test involves 96 h submersion at ambient temperature and pressure in Solution A, a sodium chloride, acetic acid solution saturated with hydrogen sulfide gas.^[23] After testing, the charged specimens were sectioned every 25 mm along the ND-TD plane to reveal cracks, as specified in NACE TM0284.^[23]

To quantify the extent of cracking in the tested specimens, the sectioned samples were mechanically ground and polished down to a 1 μ m final polish and analyzed using light optical microscopy (LOM). Cracks were measured at a magnification of 100 × in a light optical microscope using the procedure in NACE TM0284.^[23] Figure 3(c) is a schematic demonstrating the parameters used to calculate crack sensitivity ratio (CSR), crack length ratio (CLR), and crack thickness ratio (CTR).^[23] The equations for CSR, CLR, and CTR are shown below in Eqs. [1], [2], and [3], respectively, where *a* is crack length, *b* is crack thickness, *W* is section width, and *T* is specimen thickness as shown in Figure 3(c).

$$CSR = \frac{\Sigma(a \times b)}{(W \times T)} \times 100 \text{pct}, \qquad [1]$$

$$CLR = \frac{\Sigma a}{W} \times 100 \text{pct}, \qquad [2]$$

$$CTR = \frac{\Sigma b}{T} \times 100 \text{pct}, \qquad [3]$$

To measure the evolution of phase fractions, samples for Mössbauer spectroscopy were cut along the ND-TD plane using an abrasive cut-off saw, mechanically ground to approximately 100 μ m thickness using 120 grit silicon carbide (SiC) paper, then thinned to $\sim 70 \ \mu m$ thickness using 180 grit SiC paper. The samples were then polished with 1200 grit SiC paper. Lastly, the samples were thinned to a thickness ranging between 20 and 32 μ m using a 10:10:1 mixture of water, hydrogen peroxide, and hydrofluoric (HF) acid, respectively. One sample for each of the heat treatment conditions was analyzed. Mössbauer spectra were collected at room temperature using a $^{57}\mathrm{Co}\text{-Rh}$ source in the standard constant acceleration mode. Details of the experimental technique and quantitative analysis procedures are described elsewhere.^[24] X-ray diffraction (XRD) patterns were obtained from the same samples used for Mössbauer spectroscopy, and scan times were increased to accommodate the small size of the Mössbauer samples. The patterns were obtained in the standard Bragg–Brentano symmetric mode using copper X-rays. The scans were conducted from diffraction angles between 40° and 105° in 0.02° step increments. A modified Williamson-Hall analysis^[25] was used to determine the evolution of dislocation density upon tempering from the XRD data.

Secondary electron (SE) micrographs of the etched as-received (AR) steel before HIC testing were collected from random locations through thickness in order to determine the M/A line fraction. Using ImageJ, a public domain Java image processing program,^[26] random lines were drawn in the rolling direction. Figure 4(a) demonstrates the process by which the total line length (white dashed lines) was measured, in addition to the line fraction of M/A intersected by the lines (thick red lines). The NACE TM0284 tested samples in the as-received condition were also analyzed to determine the fraction of M/A associated with HIC. The specimens were first etched with 2 pct nitric acid in ethanol (nital) and then imaged in the ND-TD plane using the SE detector in a JEOL®-7000 field-emission scanning electron microscope (FESEM). In this study, M/A in SE micrographs are characterized as light-colored regions, in contrast to the darker grey ferritic matrix. The SE micrographs were analyzed using ImageJ software. The total crack length was measured, and the line length of M/A adjacent to or intersecting the crack was also measured, as shown in Figure 4(b). The ratio of M/A adjacent to the crack to total crack length was then calculated. In addition to using the line fraction measurements of M/A, electron backscatter diffraction (EBSD) was conducted on AR specimens. The samples were prepared in Bakelite mounts, then ground and polished using traditional metallurgical techniques, finishing with a vibratory polish in a $0.02 \ \mu m$ colloidal silica suspension for several hours.



Fig. 2—Schematics of the machining specifications for tensile and Charpy specimens where (a) demonstrates the orientation of the machined samples relative to the original plate directions, (b) is the machining schematic for the round sub-size ASTM E8 specimens, and (c) is the machining schematic for the Charpy specimens. Reprinted from—Ref. 20.

EBSD was collected using a JEOL®-7000 FESEM using a 20 kV accelerating voltage with a step size of 50 nm. The lattice strain-based contrast that image quality maps offer was chosen to identify M/A, where M/A is distinguished as dark, low image quality (IQ) regions due to high dislocation density. The thresholding function in ImageJ was utilized on EBSD IQ maps to calculate the area fraction of M/A,

III. RESULTS

A. NACE TM0284 HIC Test Results

Figure 5(a) shows the crack length ratio data from the NACE TM0284 test plotted against tempering temperature, including the untempered as-received (AR) X65 sample. Error bars indicate one standard deviation from



Fig. 3—Schematics demonstrating (a) the geometry and location of the samples used in the NACE TM0284 test with respect to the as-received plate, (b) the sections and sample directions analyzed for the crack analysis, and (c) the ND-TD plane analyzed for crack calculations. Reprinted from—Ref. 20.

the mean, where each condition had 9 sample faces analyzed. The AR sample exhibited the most cracking with 10.8 pct CLR. A light optical micrograph of the AR steel, etched with 2 pct nital, exhibiting the typical step-wise morphology of cracks produced by the HIC test is shown in Figure 5(b). All tempered conditions resulted in lower CLR values than the AR sample. However, the data presented in Figure 5 indicate a higher amount of cracking in the samples tempered at 400 °C than the rest of the tempered samples. The sample tempered at 400 °C also exhibited the highest standard deviation among the conditions. Table II lists CLR values calculated from each ND-TD section, demonstrating the stochastic nature of HIC. For example, of the 9 sample faces analyzed in the AR condition, five faces demonstrated no cracking while 4 faces demonstrated CLR values of ~ 20 pct. Furthermore, the 400 °C sample similarly demonstrated cracking in 4 out of 9 on the analyzed faces. However, the range of CLR values, from 9 to 45 pct, was much wider in the 400 °C sample than in any other condition, which led to the largest measure of uncertainty. Cracking occurred on 2-3 faces in the other conditions and exhibited slightly less scatter.



Fig. 4—Secondary electron micrographs demonstrating the calculation of M/A line length in the AR steel etched with 2 pct nital, where (*a*) is an example of the measurements before HIC testing where red lines indicate the line fraction of M/A and (*b*) is an example of an SE micrograph from a HIC tested sample where white arrows point to M/A constituents and white dashed lines indicate the line fraction of M/A along a crack (Color figure online).



Fig. 5—(a) Crack length ratios (percent) for the X65 AR and tempered conditions tested using NACE TM0284 HIC test (reprinted from—Ref. 20) and (b) light optical micrograph of a section of the AR steel etched with 2 pct nital after HIC testing demonstrating the typical crack morphology.

 Table II.
 Crack Length Ratio Values Calculated from Each ND-TD Sample Faces (Percent)

	A1	A2	A3	B 1	B2	B 3	C1	C2	C3
AR	0	0	26.5	0	21.5	0	0	24.8	24.4
300 °C	0	0	0	0	0	0	12.2	12.4	0
400 °C	9.3	0	44.6	0	16.3	0	0	0	16.2
500 °C	0	18.7	0	39.3	22.0	0	0	0	0
600 °C	31.9	0	0	11.0	0	0	0	0	14.5

In addition to quantifying the amount of cracking, the location of the cracks through the thickness in the AR steel was assessed. Table III presents the results of the measurements of crack locations through the thickness. The results show that five out of six, or the majority, of cracks in the AR steel are located within 25 pct of the total thickness from either surface, while only one of the cracks was observed at the centerline. The observation

Table III. Hydrogen-Induced Crack Distance from Surface in the AR X65 Steel

Crack #	1	2	3	4	5	6
Length (mm)	3.78	2.36	3.85	3.11	5.43	6.46
Distance from surface (mm)	2.22	0.86	0.86	1.28	2.09	6.35
Description of location	< 1/4	< 1/4	< 1/4	< 1/4	< 1/4	center



Fig. 6—Vickers hardness (HV0.5) as a function of tempering temperature. The "+" symbols designate one standard deviation from the mean. Reprinted from —Ref. 20.

of cracking near the surfaces also applies to the tempered conditions.

B. Mechanical Properties

The Vickers hardness as a function of tempering temperature is shown in Figure 6. Hardness of the tempered and AR conditions did not exhibit differences that were statistically significant. If only the averages are considered, tempering over the entire temperature range slightly increased hardness relative to the as-received condition, and the average hardness reached a maximum upon tempering at 300 °C followed by a small decrease (~ 10 HV) in the sample tempered at 400 °C. The average hardness slightly increased in the 500 and 600 °C tempered conditions, albeit within one standard deviation of the 400 °C hardness.

The uniaxial tension properties of the AR and tempered samples were characterized, and representative engineering stress-strain curves from each condition are shown in Figures 7(a) and (b). The average tensile properties obtained from the tensile tests are tabulated in Table IV along with Vickers hardness values. The 0.2 pct offset yield strength (YS) and ultimate tensile strength (UTS) are plotted in Figure 8. The as-received condition exhibits the highest UTS, while UTS of the tempered conditions is about 80 MPa less than the AR condition. The engineering stress–strain curves in the vicinity of the yield point are shown in Figure 7(b), where increasing tempering temperature introduces a more defined yield point starting at 400 °C. Correspondingly, the 0.2 pct offset yield strength gradually increased with increasing tempering temperature. Lastly, the total elongation of all the conditions differed by less than 3 pct, but the highest ductility was observed in the 600 °C tempered sample and the lowest ductility was exhibited in the AR sample.

Room temperature Charpy impact toughness results are shown in Figure 9(a) where absorbed energy at room temperature, hereafter referred to as impact toughness, is plotted as a function of tempering temperature. Impact toughness increased relative to the AR condition at all tempering temperatures. The peak impact toughness occurs in samples tempered at 400 °C and 500 °C, while the 300 °C and 600 °C tempering treatments resulted in intermediate impact toughness. Charpy testing was also conducted at a range of temperatures to calculate absorbed energy values as a function of testing temperature, shown in Figure 9(b), demonstrating the transitional behavior from upper to lower shelf energy for each of the sample conditions. The lines are hyperbolic tangent regression curves, obtained by least squares fitting. Using the inflection point between the upper and lower shelf energies as a measure of ductile to brittle transition temperature (DBTT), Figure 9(b) indicates that the DBTT is relatively constant between - 40 and - 60 °C for all tempering conditions, within the limited sample population used in this study.

C. Microstructure

An optical micrograph of the AR condition etched with 2 pct nital is shown in Figure 10. The microstructure in the AR condition is characterized as a mixed proeutectoid ferrite and granular bainite microstructure. Light-grey regions in light optical micrographs like Figure 10 are ferrite, while dark regions are M/A. The white outlines in Figure 10 have been added to emphasize regions characterized as granular bainite.

The area fractions of the M/A at the center and quarter thicknesses were calculated using EBSD images. Figure 11(a) and (b) are IQ maps of the AR steel from the centerline and quarter thickness, respectively, showing that the centerline region contained about 10 pct M/A (Figure 11(a)) and the quarter thickness region contained about 14 pct M/A (Figure 11(b)).



Fig. 7—Engineering stress–strain curves of the AR, 300 °C, 400 °C, 500 °C, and 600 °C tempered samples where (a) are complete engineering stress–strain curves and (b) are details of the engineering stress–strain curves in the yield point regime.

Two different characteristic morphologies of secondary constituents were observed in the AR steel, examples of which are shown in the SE micrographs of Figures 12(a) and (b). A granular bainitic region with a "blocky" M/A morphology is shown in Figure 12(a), deemed "blocky" due to the low aspect ratio of the M/ A. The second characteristic constituent morphology is shown in Figure 12(b), where the M/A has a higher aspect ratio along the horizontal direction. In both morphologies, the interface between adjacent ferrite and M/A appears smooth and continuous in the AR condition.

A micrograph containing secondary microconstituents in the 300 °C tempered steel is shown in Figure 13. The edges of the prior M/A are not smooth and continuous like those found in the AR steel (Figure 12). The increased roughness is likely associated with decomposition of M/A and occurred for both the "blocky" and high aspect ratio M/A morphologies. Despite the change in interfacial roughness, the general shape of the original M/A constituent can still be seen from the raised and light-grey appearance. Only partial decomposition of the M/A would be expected at this temperature. The light-grey, raised appearance of the islands is similar to that of the AR M/A constituents in Figures 12(a) and (b), but is different in that the 300 $^{\circ}$ C tempered steel has a significantly rougher ferrite/M/A interface.

The prior M/A in the samples tempered at 400 °C have markedly different appearances than those in the 300 °C sample, as shown in the SE micrographs in Figures 14(a) and (b). White particles assumed to be cementite in Figures 14(a) and (b), often appear at the boundaries between the ferrite and the prior M/A. Light-colored particles appear within the prior M/A in Figure 14(a), but most have precipitated at the interface with the adjacent ferrite grains. Additionally, Figure 14(b) demonstrates the presence of white particles (white arrows) in elongated morphologies at the prior M/A boundary. These white particles are assumed to be cementite based on etching relief. Complete decomposition of the retained austenite and formation of cementite is expected upon tempering at 400 °C, and likely contributed to the darker grey appearance of the interior of the prior M/A regions. Additionally, it should be noted that elongated cementite shapes occurred more often in the elongated M/A morphology (Figure 14(b)) than in the "blocky" morphology (Figure 14(a)).

"Blocky" and high aspect ratio M/A morphologies, easily discernable in the AR, 300, and 400 °C conditions, are less discernable in samples tempered at 500 and 600 °C. Figure 15(a) is a SE micrograph of the 500 °C tempered steel etched with 2 pct nital, which includes a "blocky" prior M/A (outlined in white), demonstrating precipitation both within the prior M/A and within the adjacent ferrite grains. Lastly, a SE

Table IV. Average Tenshe Flobernes and vickets flatuness values (fivu	Table IV.	Average	Tensile	Properties	and Vickers	Hardness	Values	(HV0.:
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	0.2 pct Offset YS (MPa) [ksi]	UTS (MPa) [ksi]	Hardness (HV0.5)	Uniform Elongation (Percent)	Total Elongation (Percent)
AR	479 [69.5]	735 [107]	209	11.0	26.8
300 °C	513 [74.4]	650 [94.3]	224	10.3	28.8
400 °C	553 [80.2]	628 91.0	214	10.5	28.5
500 °C	544 78.9	637 [92.4]	216	10.5	27.8
600 °C	584 [84.7]	668 [96.9]	221	10.5	29.2



Fig. 8—Average UTS and YS values calculated using engineering stress-strain data from uniaxial tensile tests as a function of tempering temperature.

micrograph of the 600 °C tempered X65 steel is shown in Figure 15(b), with a magnified inset. Upon tempering at 600 °C, the entire matrix is dark-grey, consistent with ferrite, with rounded white particles distributed along boundaries. The distinction between "blocky" and high aspect ratio prior M/A is less significant, as expected at this high tempering temperature due to the extensive decomposition of retained austenite (RA) and martensite to ferrite and cementite.

D. Phase Fractions and Dislocation Density

Results from Mössbauer spectroscopy demonstrating the relative phase amounts as a function of tempering temperature are shown in Figures 16(a) and (b). Mössbauer results are shown in units of atomic percent

iron (at. percent Fe) attributed to each respective phase, *i.e.*, austenite, magnetic cementite, and non-magnetic cementite. It should be noted that no transition carbides were detected by Mössbauer as a result of any of the tempering treatments. Retained austenite (open triangles in Figure 16(a)) was ~ 2 at. pct Fe in the AR condition, which decreased to 0.3 at. pct Fe upon tempering at 300 °C, and decreased further below detectable limits at tempering temperatures 400 °C and above. In contrast, the fraction of magnetic cementite (solid circles in Figure 16(a)) in the AR sample was less than 0.25 at. pct Fe, and increased to ~ 0.5 at. pct Fe upon tempering in the 300 °C, 400 °C, and 500 °C conditions. At 600 °C, the magnetic cementite phase fraction (solid circles in Figure 16(a)) decreased relative to that measured in the 500 °C tempered sample. However, the combined magnetic and non-magnetic cementite fractions (open circle in Figure 16(a)) was ~ 0.5 at. pct Fe total. The presence of non-magnetic cementite has been observed in the 600 °C tempering range in other steel systems,^[12] and has been attributed to substitutional diffusion of manganese into the cementite lattice.^[27] In addition to phase fraction, the amount of carbon in solution in retained austenite was calculated from the Mössbauer data,^[28] and the values of carbon in austenite are shown in Figure 16(b), compared to the nominal steel value. While the nominal carbon composition of the steel was 0.23 at. pct, the average carbon in austenite was ~ 4 at. pct (0.865 wt pct) in the AR condition and did not statistically significantly increase upon tempering at 300 °C. Carbon enrichment of the austenite would be expected during the intercritical finish rolling step.

X-ray diffraction patterns were obtained for the AR and tempered conditions of the steel to quantify the evolution of dislocation density upon tempering. A modified Williamson-Hall^[25] approach was used to analyze the data. Figure 17 demonstrates the evolution of dislocation density upon tempering. As expected, the dislocation density decreases with increasing tempering temperature.



Fig. 9—Results from Charpy impact testing where (a) is room temperature absorbed energy (impact toughness) from Charpy testing as a function of temperature and (b) is absorbed energy as a function of testing temperature for all sample conditions where the lines are hyperbolic tangent regression curves.



Fig. 10—Light optical micrograph of the AR condition etched with 2 pct nital, with white outlines added indicating regions of granular bainite containing ferrite and M/A. Reprinted from—Ref. 20.

IV. DISCUSSION

Understanding HIC behavior of the AR and tempered conditions necessitates a discussion of the origin and evolution of the observed microstructures. During intercritical finish rolling, both austenite and ferrite coexist during deformation. Solute elements such as carbon and manganese partition out of ferrite and into adjacent austenite during intercritical finish rolling. Figure 18 is a schematic demonstrating solute enrichment of austenite grains due to formation of proeutectoid ferrite during intercritical rolling. It is suspected that the elongated M/A morphologies originate during intercritical finish rolling. The enriched austenite grains then transform to granular bainite upon accelerated cooling. The M/A area fraction was shown to vary through thickness (Figure 11), with a higher area fraction of M/A at the quarter thickness than at the centerline. Both compositional variation and cooling rate variation through thickness likely contributed to the difference in M/A area fraction observed between center and quarter thicknesses.

The change in phase fraction with tempering in this work is similar to the behavior observed in fully martensitic steels. Just as in fully martensitic steels, retained austenite dissolved partially upon tempering at 300 °C and completely at higher tempering temperatures. The volume fraction of cementite that formed upon tempering at 300 °C was equivalent to the other tempering conditions, although a fraction became non-magnetic due to manganese substitution in the 600 °C tempered sample. Unlike fully martensitic steels, no transition carbides were measured by Mössbauer in the 300 °C tempered samples, which likely indicates that any χ Hagg, η , or ε carbides that might have been present were replaced by cementite during tempering at 300 °C. Microstructural observations of the steels etched with 2 pct nital generally supported the Mössbauer phase fractions results and contributed morphological understanding. For instance, elongated M/A morphologies in the AR condition seemed to have a propensity to preferentially form elongated cementite. It is possible that the elongated M/A and cementite morphologies exacerbated cracking in the AR and 400 °C conditions,



Fig. 11—EBSD IQ maps from the AR condition with calculated M/A area fractions overlaid, where (*a*) is a micrograph from the centerline and (*b*) is from the quarter thickness. M/A constituents are identified as black regions in the micrographs.



Fig. 12—SE micrographs of the AR condition etched with 2 pct nital demonstrating two different characteristic constituent morphologies where (a) demonstrates "blocky" M/A while elongated M/A is shown in (b). Reprinted from—Ref. 20.

but an in-depth study of the effect of microconstituent morphology on cracking is not the focus of the current study.

Although the phase fraction evolution was similar to what would be expected in fully martensitic steels, the trend in tensile properties and hardness is more similar to that observed in dual phase steels.^[29,30] Only 15 pct of the microstructure (M/A volume fraction) in the X65

steel would be significantly affected by tempering from 300 to 600 °C. Yield strength increases with increasing tempering temperature, largely due to more pronounced discontinuous yielding after tempering at higher temperatures, as shown in Figure 7(b). Values for UTS are similar for all the tempered specimens (~ 650 MPa) which is lower than UTS in the AR condition (735 MPa). The decrease in UTS upon tempering at

300 °C is likely attributed to dislocation density decrease (Figure 17), recovery in M/A constituents (Figure 16(a)), and partial decomposition of RA (Figure 16(a)). Dislocation density continues to decrease with increasing tempering temperature, which would result in a large decrease in strength and hardness in fully martensitic steels. However, the reduction in strength due to decreasing dislocation density occurs simultaneously with the microalloy precipitation that increases strength, particularly at 500 °C and 600 °C. The net effect of strengthening and softening results in



Fig. 13—SE micrographs of the 300 °C tempered steel etched with 2 pct nital demonstrating increased roughness at the boundary of the prior M/A and adjacent ferrite. Reprinted from—Ref. 20.

the constant UTS trend with increasing tempering temperature observed in Figure 8.

Tempering improved room temperature impact toughness significantly relative to the AR condition, much like what has been observed in fully martensitic steels. The 300 °C condition exhibited higher room temperature toughness than the AR condition, 350 J and ~ 225 J, respectively, likely due to a decrease in dislocation density. Increases in impact toughness relative to the AR condition are expected when tempering microstructures with any amount of martensite, as well as a reduction in UTS, as was observed in the current study. Impact toughness increases again from 350 J (300 °C condition) to \sim 430 J in the 400 and 500 °C conditions, and this could be due to a combination of the complete dissolution of RA and an additional decrease in dislocation density. The 600 °C tempered sample exhibited the lowest impact toughness of all the tempered conditions, although the reason for the relatively low impact toughness was not investigated. It is important to note that no tempered martensite embrittlement regime was identified upon tempering in this study. The deleterious impact of M/A constituents on impact toughness has been well-docu-mented in literature,^[3,31,32] so it is unsurprising that the decomposition of M/A led to an increase of impact toughness in the current study.

In addition to affecting impact toughness, M/A constituents are often associated with HIC. To assess the role of M/A in HIC in the AR steel, the ratio of M/A -crack interactions to total hydrogen-induced crack length was measured, as was the line fraction of M/A along the rolling direction in the AR samples before HIC testing. Table V tabulates the total line lengths examined, the total line length adjacent to or



Fig. 14—SE micrographs of the 400 °C tempered steel etched with 2 pct nital demonstrating both (a) "blocky" and (b) elongated prior M/A morphologies where the arrows indicate elongated boundary cementite. Reprinted from—Ref. 20.



Fig. 15—SE micrographs of (a) the 500 °C tempered steel etched with 2 pct nital demonstrating precipitation both within prior M/A (outlined in white) and in adjacent ferrite (reprinted from—Ref. 20), and (b) the 600 °C tempered sample demonstrating cementite precipitation along boundaries and a lack of discernable prior M/A.



Fig. 16—(a) Phase amounts in atomic percent Fe from Mössbauer analysis as a function of tempering temperature. (reprinted from—Ref. 20) (b) The amount of carbon in solution in austenite calculated from Mössbauer spectroscopy. Above 300 °C, the amount of austenite was too small to determine carbon content.

intersecting M/A, and the percentage of the line length that is adjacent to or intersecting an M/A constituent. The line fraction of M/A in the as-received microstructure was measured to be 15.2 pct. The line fraction of M/A calculated with this methodology aligns well with the area fractions of M/A measured using EBSD in Figures 11(a) and (b) (10 to 14 pct, respectively). In contrast, the line fraction of M/A interactions along the

total crack length was 25.4 pct. The observation that the line fraction of M/A interactions along cracks is greater than the M/A line fraction in the microstructure of the AR steel could indicate that M/A contributes to HIC susceptibility.

Pipeline steels are often reported to have higher M/A area fractions at the centerline due to chemical segregation during continuous casting,^[14,33,34] which is,

in turn, associated with a preference for HIC to form at the centerline.^[35–37] Both the M/A area fraction, and cracking, in the current study was highest between the surface and quarter thickness, which strengthens the supposition that M/A exacerbates cracking in this steel. The mechanism by which M/A influences HIC susceptibility is still not well understood, but the internal hydrogen pressure theory is most often employed to explain HIC phenomena. In this theory, hydrogen gas accumulates at microstructural trap sites, like those present in M/A, until the



Fig. 17—Dislocation density as a function of tempering temperature as measured using XRD and analyzed using the Williamson-Hall method. Reprinted from—Ref. 20.

concentration exceeds some local maximum, resulting in formation of voids and propagation of cracks. Examples of microstructural trap sites in M/A constituents include a high density of dislocations, austenite which has a high solubility for hydrogen, and microalloy precipitates. If the internal hydrogen pressure theory is applied to the steel in the current study, the high dislocation density and austenite within M/A constituents would act as sites for hydrogen accumulation and subsequent crack formation. Subsequently, tempering would reduce the propensity for hydrogen accumulation and subsequent cracking by decreasing the number of microstructural traps in M/A (dislocations and austenite). Lastly, it is interesting to note that trends in strength/hardness are dominated by the ductile majority phase, while trends in impact toughness and HIC susceptibility are dominated by characteristics of the minority constituent (M/A). This observation could inform which mechanical properties would best be suited to predict HIC susceptibility.

Table V. INTA Line Flaction Values of As-Accelieu Ste

	AR NACE TM0284 Specimens	As-received
Total line/crack length (μ m)	410	741
Total M/A line length (μ m)	104	122
Ratio of M/A interactions to total line length (percent)	25.4	15.2



Fig. 18—Schematic demonstrating the formation of elongated M/A based on solute segregation from proeutectoid ferrite to the remaining austenite during intercritical rolling prior to accelerated cooling. Reprinted from—Ref. 20.

An intercritically rolled X65 linepipe steel was assessed for HIC susceptibility in both the as-received condition and after tempering for 40 min at temperatures ranging from 300 to 600 °C. Results of NACE TM0284 HIC tests indicated that the steel was most susceptible to HIC in the as-received state, indicating that tempering successfully reduced HIC susceptibility within the range of temperatures used in this study. Moreover, tempering improved impact toughness and vield strength. Mössbauer spectroscopy and dislocation density measurements from XRD demonstrated retained austenite decomposition, cementite formation, and dislocation density reduction, similar to that of fully martensitic steels. Microalloy precipitation at 500 °C and 600 °C is suspected to have contributed to the stability of hardness and UTS values despite decreasing in dislocation density.

The relative stability of YS, UTS, and hardness over a wide range of tempering temperatures was attributed to the reliance of these properties on the majority phase, ferrite, which was relatively unaffected by tempering at these temperatures. Small changes observed in YS, UTS, and hardness were attributed to dislocation density reduction, dislocation pinning by carbon, RA decomposition to cementite, and microalloy precipitation. In contrast, the significant improvement of HIC resistance and impact toughness was attributed to the decomposition of deleterious M/A constituents. The current work demonstrates the potential to use tempering of thermo-mechanically processed linepipe steels to reduce HIC susceptibility and increase impact toughness while maintaining strength and hardness.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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