6.1 Introduction

This research project, funded by the U.S. Department of Energy (DOE), was initiated in September 2020 as a Ph.D. project for Yuran Kong in the Metallurgical and Materials Engineering Department at the Colorado School of Mines. The primary objectives of this project are as follows:

(a) to develop low-cost alternatives to the expensive high nickel (Ni)-containing austenitic stainless steels currently used in hydrogen (H) storage and transportation infrastructure and

(b) to develop and validate accelerated testing methods to evaluate H compatibility of steels in various alloy and microstructural conditions.

Austenitic stainless steels are widely used in current H infrastructure due to their excellent H compatibility partly because of their austenitic microstructure, which is known to be more resistant to H embrittlement (HE) compared to a ferritic microstructure. However, these steels contain a large quantity of expensive Ni, which contributes to the economic barrier in constructing H infrastructure. The current project aims at providing economical alternatives to high Ni austenitic stainless steels. One strategy that is being explored in this project is to replace Ni with manganese (Mn), which is also a powerful austenite stabilizer but about 80 pct cheaper than Ni [6.1]. Two different microstructural design concepts have been proposed to achieve the primary objectives of the DOE H2@Scale Program at Colorado School of Mines: fully austenitic and austenite-ferrite (martensite) duplex microstructures. The strategy with a fully austenitic microstructure is being investigated by P. Kathayat for his Master of Science Program while the current project for Kong’s Ph.D. program focuses on the duplex alloy strategy.

In previous reports [6.2, 6.3], the alloy design concepts for high Mn duplex steel development were proposed to fulfill the first primary objective, i.e., developing economical materials for H service. The alloy design was guided by a literature review on the effects of alloying on austenite stacking fault energy (SFE), which is established to be correlated with the mechanical stability of austenite and HE resistance. The composition of the high Mn duplex steel was designed considering the SFE (SFE \( \geq 45 \text{ mJ} \cdot \text{m}^{-2} \)) and equilibrium volume fraction of austenite in duplex microstructures \( f_{\gamma,RT} \approx 70 \text{ pct} \), obtained through thermodynamic calculations. As for the second objective, the development of accelerated HE testing with electrochemical H charging methods was initiated utilizing a 255 duplex stainless steel as the reference material. The electrochemical charging method is intended to be a surrogate for testing in gaseous hydrogen at a pressure of approximately 103 MPa. This part of the project is being performed in collaboration with Sandia National Laboratories-Livermore (SNL). The duplex stainless steel specimens were tested in electrochemical H environments at Mines and in gaseous H environments at SNL. In the previous reporting period [6.3], the mechanical properties of the duplex stainless steel specimens tested in various electrochemical H environments were compared with those tested in gaseous H environments. In that work [6.3], the
notch tensile strength (NTS) values obtained under electrochemical charging conditions with 0.05 M NaOH aqueous solution were generally close to those from gaseous H charging (provided by SNL).

The current report reviews literature related to the effects of microalloying additions on the HE resistance of medium-Mn duplex steels. The microstructures and microhardness of the designed V-microalloyed high Mn steel were analyzed in the as-rolled and heat-treated conditions. Fractographic analyses were performed on circumferentially notched tensile (CNT) specimens of the duplex stainless steel tested to failure in electrochemical H environments at Mines, compared to those tested in gaseous H charging environments at SNL.

6.2 Industrial Relevance

Two major obstacles to the broader use of hydrogen energy technologies include (1) cost and reliability of H storage and delivery infrastructure; and (2) cost and complexity of evaluating materials in hydrogen environments. In particular, the ferrous alloys known to have high resistance to HE, e.g., high Ni-containing austenitic stainless steels, are relatively expensive. The current study aims at overcoming the first obstacle by designing Mn-alloyed duplex steels that offer comparable performance in H environments and cost less compared to high Ni austenitic stainless steels. In addition, this study will identify alloy and microstructural conditions with an enhanced combination of strength (in the range of 400-800 MPa) and toughness in H. Gaseous hydrogen charging is the charging methodology best representing gaseous hydrogen service in practice. However, the testing method is expensive, complicated, and thus, not widely available. To resolve this obstacle, the current study also focuses on the development and validation of electrochemical H charging methods utilizing a 255 duplex stainless steel as a reference material.

6.3 Literature Review

Microalloying involves adding small quantities (about 0.01 – 0.15 wt pct) of alloy elements such as Nb, V, and Ti to a base alloy. Previous studies have shown that microalloying additions can enhance the yield strength and toughness of medium Mn steels via grain refinements and precipitation hardening. For example, Pan et al. [6.4] investigated the influence of microalloying additions (0.05 wt pct Nb and 0.22 wt pct Mo) on the microstructure and mechanical properties of a medium Mn steel (Fe-6Mn-0.2C-1Al, all in wt pct). They reported that the Nb and Mo additions resulted in decreases in retained austenite grain sizes and volume fractions after annealing, which led to higher austenite stability and increased strength without sacrificing ductility.

Microalloying with Ti, Nb, and V, which results in the precipitation of H-trapping carbides like MC carbides, is known to reduce HE, at least in ferritic steels. In this regard, Park et al. [6.5] explored the possibility of utilizing microalloying to improve the HE resistance of medium Mn steels in the cold-rolled state. In the study by Park et al., 0.01 to 0.10 wt pct of Ti, Nb, or V was added to a base alloy (Fe-6.13Mn-0.08C-0.28Al-0.11Si, all in wt pct); the chemical compositions of the investigated alloys are listed in Table 6.1. Figure 6.1(a) and (b) show the microstructural characteristics of each alloy condition concerning grain sizes and phase fractions. Adding microalloying elements generally resulted in increases in retained austenite (γ\text{R}) volume fraction, and refinement of both ferrite (α) and γ\text{R} grain sizes. Figure 6.1(c) shows the tensile properties of each alloy in the H-free condition. All microalloyed steels showed higher yield strength and ultimate tensile strength compared to the base alloy at the
expense of total elongation. The authors attributed the increased strength levels to precipitation hardening and finer grain size of \(\alpha\) ferrite [6.5].

Table 6.1 – Chemical Compositions (in wt pct) of the Base Steel and Microalloyed Variants [6.5]

<table>
<thead>
<tr>
<th>Steels</th>
<th>Mn</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>Nb</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>6.13</td>
<td>0.08</td>
<td>0.28</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H_Ti</td>
<td>6.38</td>
<td>0.08</td>
<td>0.29</td>
<td>0.12</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L_Ti</td>
<td>6.33</td>
<td>0.08</td>
<td>0.31</td>
<td>0.12</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H_Nb</td>
<td>6.41</td>
<td>0.08</td>
<td>0.30</td>
<td>0.12</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>L_Nb</td>
<td>6.10</td>
<td>0.08</td>
<td>0.26</td>
<td>0.11</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>H_V</td>
<td>6.44</td>
<td>0.08</td>
<td>0.31</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>L_V</td>
<td>6.38</td>
<td>0.08</td>
<td>0.31</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Figure 6.1  
(a) Volume fraction of retained austenite \((\gamma_R)\) in base and microalloyed medium Mn steels, determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Table 6.1 lists the chemical compositions of the steels. (b) Grain sizes of \(\gamma_R\) and ferrite \((\alpha)\) in each alloy determined by SEM. (c) Engineering stress-strain curves of each alloy tested in the non-charged condition [6.5]. (Color images – See PDF version)

Figure 6.2 shows the reduction in total elongation for each alloy condition after electrochemical pre-charging with H for 1 h or 3 h. Except for one condition (0.10 wt pct Nb-added alloy charged for 3 h), the microalloyed steels showed slightly lower percentages of elongation losses compared to the base alloy, indicating
small improvements in HE resistance due to the microalloying additions, in combination with higher strength levels. The authors explained that the effect of microalloying on increasing HE resistance was generally not significant for the medium Mn steels because microalloy precipitates formed primarily in $\alpha$ phase, while diffusible H atoms are mostly contained in $\gamma_R$ phase, where H is more soluble than in ferrite. They further hypothesized that during deformation of the H-charged samples, the H-enhanced $\gamma_R$ phase transformed to mechanically induced martensite, releasing trapped H atoms to the grain boundaries. Therefore, H-assisted cracks initiated primarily and propagated along the boundaries, leading to premature fracture. Overall, Park et al. [6.5] appear to have interpreted the observed embrittlement in the context of the H-induced decohesion (HEDE) mechanism [6.6].

Figure 6.2  Loss of total elongation of the base alloy and microalloyed steels in tension after H charging for 1 h or 3 h [6.5]. (Color images – See PDF version)

There is limited information in the literature on the microalloying effect on HE resistance of Mn-alloyed duplex steels, except for the above-referenced study [6.5]. It is thought that the beneficial effect of microalloy precipitates might be more important for specific microstructures or alloy compositions. For example, Sun et al. [6.6] studied the microstructure-driven H distribution and HE mechanisms in a cold-rolled medium Mn duplex steel (Fe-0.2C-10.2Mn-2.8Al-1Si, all in wt pct) with two different heat treatment conditions. The authors reported that the H distribution within the ferrite-austenite microstructures depended on the heat treatment and resulting microstructural morphologies. Particularly in one of the two heat treatment conditions, most H atoms were trapped in the $\alpha$ ferrite phase. Furthermore, for a 2205 duplex stainless steel [6.7], H-induced cracks have been reported to form preferentially within ferritic grains, in contrast to the observations reported by Park et al. [6.5]. In these circumstances, the microalloying effect on HE mechanisms could be different from the results reported by Park et al.
6.4 Experimental Procedure

This section presents the materials, specimen geometries, and experimental procedures to explore the effect of heat treatment on the microstructures and hardness of the designed high Mn duplex steel. HE testing and fractographic analysis procedures are also described.

6.4.1 Materials

The target and actual chemical composition (in wt pct) of the high Mn duplex steel, produced with the support of U.S. Steel, are shown in Table 6.2. The estimated austenite SFE is also included in Table 6.2, which was calculated assuming a single-phase austenite having the bulk composition of the steel; in reality, the actual SFE of austenite in the duplex microstructure is affected by heat treatment and would likely be higher than the estimated value depending on the elemental partitioning between ferrite and austenite. Austenite SFE is known to be correlated with the mechanical stability of austenite and HE resistance. According to a study by Gibbs et al. [6.8], an austenitic stainless steel with an SFE higher than 39 \( \text{mJ} \cdot \text{m}^{-2} \) generally has acceptable H compatibility; in general, an austenite SFE higher than 45 \( \text{mJ} \cdot \text{m}^{-2} \) leads to perfect dislocation glide as the dominant deformation mechanism, rather than deformation twinning or mechanically induced martensitic transformations, which is known to be detrimental to H resistance. Although the austenite SFE calculated for the actual alloy composition is slightly lower than that of the target composition, it satisfies the SFE criterion (39 \( \text{mJ} \cdot \text{m}^{-2} \)) proposed by Gibbs et al. [6.8], which is expected to result in dislocation gliding as the dominant deformation mechanism at room temperature.

Table 6.2 – Target and Actual Chemical Compositions in wt pct and Estimated Austenite SFE of the High Mn-Al Duplex Alloy, Produced by U.S. Steel. (LAP stands for “low as possible”)

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Al</th>
<th>V</th>
<th>S</th>
<th>N</th>
<th>SFE (mJ·m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>Bal.</td>
<td>0.15</td>
<td>20</td>
<td>6.0</td>
<td>0.1</td>
<td>LAP</td>
<td>LAP</td>
<td>47.7</td>
</tr>
<tr>
<td>Actual</td>
<td>Bal.</td>
<td>0.12</td>
<td>20.9</td>
<td>5.8</td>
<td>0.10</td>
<td>0.014</td>
<td>&lt;0.002</td>
<td>45.5</td>
</tr>
</tbody>
</table>

The steel ingot with the composition shown in Table 6.2 was solutionized at 1200 °C for 2 h before hot rolling by U.S. Steel into a plate with a thickness of approximately 15 mm. The finish rolling temperature was approximately 1000 °C. The hot-rolled plate was water-quenched immediately after finish rolling to preserve the duplex microstructure and perhaps some deformation substructure present after finish rolling at 1000 °C, while minimizing the formation of precipitates. The hot-rolled material was cut into two plates with dimensions of about 203 mm (8 in) in width, 406 mm (16 in) in length, and 15 mm (0.6 in) in thickness. The rationale for selection of the hot-rolling conditions was explained in the previous report [6.3].

One of the primary goals of the DOE H2@Scale program is to develop and validate electrochemical charging methods as a surrogate accelerated testing method for gaseous H environments. For the collaborative research between Mines and SNL to achieve the project goal, a 255 duplex stainless steel was selected for investigation. The chemical composition is shown in Table 6.3. SNL provided the duplex stainless steel bar material, which had a length of 226 mm and a diameter of 63.5 mm in the as-received condition.
Table 6.3 – Chemical Composition of 255 Duplex Stainless Steel (in wt pct)

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt pct</td>
<td>Bal</td>
<td>25.9</td>
<td>6.21</td>
<td>3.28</td>
<td>1.56</td>
<td>0.87</td>
<td>0.38</td>
<td>0.018</td>
<td>0.16</td>
</tr>
</tbody>
</table>

6.4.2 Heat treatments, Microstructural Analyses, and Hardness Testing

Heat treatment conditions for the high Mn duplex steel were determined using Thermo-Calc® and dilatometry results obtained using a TA Instruments DIL-805L quench dilatometer. The dimensions of the dilatometry specimen were 4.0 mm in width and thickness, and 10 mm in length. The dilatometry specimen was heated to 1100 °C at a heating rate of 0.05 °C · s⁻¹, followed by quenching with argon gas. Small coupons with dimensions of approximately 12.7 mm x 25.4 mm x 15 mm were also sectioned from the steel plate using a bandsaw. The steel coupons were heat-treated using box furnaces at temperatures of 500 °C, 600 °C, 700 °C, 900 °C, and 1100 °C for 1 h, prior to water quenching.

Heat-treated steel coupons were sectioned and hot mounted in Bakelite for microstructure analysis. Each metallography sample was mechanically ground and polished with a fine polishing step using a 1 μm diamond suspension. The microstructure was revealed by etching in 4 pct nital solution for approximately 10 s. The microstructures of the as-rolled and heat-treated samples of the high Mn duplex steel were analyzed using an Olympus® DSX500 light optical microscope (LOM). The microhardness values of these samples were measured using a LECO® AMH55 automated hardness indenter. The load used for the hardness measurements was 25 gf or 50 gf, depending on the grain (or island) sizes of austenite and ferrite. At least 9 individual tests were performed for each phase for each alloy condition.

6.4.3 Mechanical Test Specimen Preparation

Subsize tensile specimens were machined from the plates of the high Mn duplex steel in two different orientations, i.e., with the tensile axis parallel to either the rolling direction (RD) or transverse direction (TD). A drawing of the tensile specimens is shown in Figure 6.3. The tensile specimen had a gauge length of 25.4 mm and a gauge diameter of 3.8 mm.

Figure 6.3 Schematic drawing of the tensile specimen. Dimensions are in mm.

Circumferentially notched tensile (CNT) specimens with two different geometries were machined from the duplex stainless steel bar such that the tensile axis was parallel to the longitudinal direction of the bar. The geometries and dimensions of the large and small CNT specimens are shown in Figures 6.4 and 6.5, respectively. The large CNT has a major diameter of 12.7 mm (0.5 in) and a minor diameter, measured at the circumferentially
notched area, of 8.00 mm (0.315 in). The notch radius of the large CNT is 0.086 mm (0.003 in); in this condition, the stress concentration factor (K_{t}) is estimated to be 6 or greater [6.9]. Lee et al. [6.10] reported that CNT specimens with a K_{t} of 6 or greater produced fracture toughness values comparable to fracture toughness from fatigue pre-cracked compact tension specimens. In addition, they pointed out that the CNT specimen geometry has an advantage in achieving plane strain conditions with a much smaller thickness compared to compact tension specimens [6.10].

Figure 6.4  Schematic drawing of the large CNT specimen used for mechanical testing utilizing electrochemical H charging at CSM. Dimensions are in mm.

A drawing of the small Mines CNT specimen is shown in Figure 6.5. The small CNT has a major diameter of 6.35 mm (0.25 in), i.e., the diameter of the smooth section adjacent to the notch area, and a minor diameter of 4.064 mm (0.160 in). The notch radius of the small CNT is 0.127 mm (0.005 in), yielding a K_{t} in the range of 3.9 to 4.2 [6.11]; i.e., this stress concentration factor is smaller compared to the large CNT specimen geometry. The CNT specimen used at SNL is shown in Figure 6.6. Both small CNT specimens (Mines and SNL) use the same notch geometry and length of the reduced section, so can be used for direct comparison of HE characteristics in electrochemical charging (Mines) versus gaseous charging environments (SNL). Note that SNL also utilized arc-shape fracture test specimens to characterize the HE characteristics of the duplex stainless steel, and they have provided the test results and fractured specimens to Mines. The test results on arc-shaped specimens are not presented here and will be reported in the next reporting period.
6.4.4 Mechanical Testing in Air and H Environments and Fractography

Room temperature tensile testing was performed in air with a screw-driven MTS® Alliance RT/100 load frame using a 20,000 lb load cell. The load frame displacement rate was 0.03 mm·min⁻¹. A 25.4 mm knife blade-type extensometer was used to record displacement during the tensile tests.

An in situ rising displacement testing technique with direct current potential drop (DCPD) measurement was used as the primary tool to evaluate the notched tensile properties of the duplex stainless steel in air and electrochemical H charging conditions. Mechanical testing was performed with a screw-driven MTS® Alliance RT/100 load frame using a 20,000 lb load cell. The load frame displacement rate was 0.005 mm·min⁻¹ (0.0002 in·min⁻¹). A 10 mm knife blade-type extensometer was used to record the displacement for specimens tested in air. Both small and large CNT specimens were tested in a 0.05 M NaOH aqueous solution with various current densities: 0.83 mA·cm⁻², 1.65 mA·cm⁻², and 5.00 mA·cm⁻². The uncertainty was estimated to be ± 0.17 mA·cm⁻² considering experimental variations in the actual area of samples exposed to the charging solution and the uncertainty in applied current. A schematic of the current and voltage probes connected to a CNT specimen for DCPD measurements is shown in Figure 6.7. Two 24-gauge wires were spot-welded on either side of the notch to supply current (indicated by blue points in Figure 6.7(a)). A total of four 30-gauge wires were spot welded on either side of the notch to measure the voltage across the notch; the purpose of two of the wires (indicated by black points in Figure 6.7(a)) was to measure the variation in voltage across the notch while the other two (green colored points in Figure 6.7(a)) were used to record the reference voltage. A BK Precision 9130 power supply was attached to the two current probes to supply a constant direct current of 1A throughout the test. A Keysight 34420A nanovoltmeter was attached to the four voltage probes. The voltage ratios were recorded every 10 s throughout the test to monitor the changes in resistance at the notch as the cross-section changed due to crack growth.

Gaseous H charging was performed at SNL at a pressure of 103 MPa. Thermal H pre-charging at a temperature of 300 °C was conducted by SNL in gaseous H at a pressure of 138 MPa to allow more redistribution of H in the austenite. After pre-charging, the specimens were placed in a freezer at -55 °C until tested in air.
Fractographic analyses were performed on the tested CNT specimens for selected conditions, each of which included results from electrochemical charging, thermal pre-charging and pressurized gas charging. After HE testing in air or under electrochemical charging conditions, the fracture surfaces of the small CNT specimens were ultrasonically cleaned in ethanol. Fractographic analyses on the two small CNT specimen types (one produced at Mines and the other provided by SNL) were performed in a JEOL® 7000 field emission-scanning electron microscope (FESEM) with an accelerating voltage of 20 kV and a working distance of approximately 25 mm. Fractured large CNT specimens were analyzed using a Raman® Tescan S8252G SEM/focused ion beam (FIB) with an Everhart–Thornley (E-T) detector and a backscattered electron (BSE) detector.

6.5 Results and Discussion

This section presents and discusses the results of dilatometry, thermodynamic calculation, microstructure, and microhardness analysis for the designed high Mn duplex steel. Fractographic analysis results are also presented for the duplex stainless steel specimens with various notch geometries and test conditions.

6.5.1 Thermodynamic Calculation, Dilatometry, and Heat Treatment Conditions

Figure 6.8(a) shows the equilibrium volume fraction of each phase for a Fe-0.115C-20.9Mn-5.81Al-0.102V (all in wt pct) steel, equivalent to the actual composition of the designed high Mn duplex steel, as a function of temperature. The equilibrium calculations were performed using Thermo-Calc® thermodynamic software. In Figure 6.8(a) at 500 ℃, austenite, ferrite, and MC carbide are thermodynamically stable. Here, the MC carbide is essentially vanadium carbide. As the temperature is increased into the range of 600 ℃ to 700 ℃, α-ferrite is completely replaced by austenite at equilibrium, and MC carbide is still stable. Further increasing the temperature above 900 ℃, δ-ferrite is stabilized in addition to austenite, while MC carbide is fully dissolved.

Figure 6.8(b) presents a dilatometry curve showing the relative length change of the high Mn duplex steel sample as a function of temperature during heating to 1100 ℃ at a rate of 0.05 ℃·s⁻¹, followed by rapid cooling with
argon gas. The dilatometry result indicates that below 590 °C, the heating curve was approximately linear, indicating a nearly constant thermal expansion coefficient, i.e., phase transformation was limited below 590 °C. In the temperature range of 590 °C to 870 °C, volume contraction, most likely associated with ferrite-to-austenite transformation, was clearly noted in the heating segment of the curve. Note that this temperature range approximately matches the range where only austenite (or with MC phase) remains stable at equilibrium (Figure 6.8(a)). In Figure 6.8(b), above 870 °C, the heating curve again becomes nearly linear most likely because the driving force for continued austenitic transformation is gradually lowered with stabilization of ferrite (δ). The relative length change was approximately linear during the subsequent Ar cooling. Since transformation was not apparent during cooling, the austenite fraction in the specimen was presumably greater than in the initial condition.

**Figure 6.8**
(a) Equilibrium volume fraction of each phase for an Fe-0.115C-20.9Mn-5.81Al-0.102V alloy (all in wt pct) as a function of temperature, calculated using Thermo-Calc® software. MC in the calculation is associated with vanadium carbides. (b) Relative change in sample length as a function of temperature, obtained from dilatometry during heating to 1100 °C, followed by Ar cooling. *(Color images – See PDF version)*

Based on the thermodynamic calculations and dilatometry results, five different annealing temperatures of 500, 600, 700, 900, and 1100 °C were selected to study microstructural evolution in the high Mn duplex steel during heat treatment. For all heat treatments, a hold time of 1 h was used. The three lower annealing temperatures (500, 600, and 700 °C) were selected to explore the effect of precipitate strengthening associated with vanadium carbides in addition to phase fraction evolution. The two higher temperatures (900 and 1100 °C) were chosen to accelerate the kinetics of solute partitioning and transformation at the temperatures where δ-ferrite is stabilized according to the thermodynamic calculation. Note that for the high Mn duplex alloy investigated in this study, δ-ferrite is likely harder than austenite, as will be discussed in Section 6.5.2, and thus the phase fractions are a key metallurgical factor to control the strength level. On the other hand, it should be noted that at higher temperatures, the grain coarsening rate is faster, which is likely not ideal in terms of optimizing the microstructure and mechanical performance.
6.5.2 Microstructure and Microhardness of the Designed High Mn Duplex Steel

Figure 6.9 shows LOM micrographs of the as-rolled microstructure of the high Mn duplex steel (Fe-0.115C-20.9Mn-5.81Al-0.102V, all in wt pct). The microstructures analyzed in the RD-ND plane and the TD-ND plane are shown in Figure 6.9(a) and (b), respectively. The as-rolled condition exhibited a duplex microstructure consisting of austenite and δ-ferrite grains, both elongated in the RD. Typically, the regions interpreted to be austenitic contained straight features (marked by arrows in Figure 6.9(a) and (b)), which are likely the boundaries of annealing twins in austenitic grains.

![LOM micrographs](image)

Figure 6.9 LOM micrographs of the as-rolled microstructure of the designed high Mn duplex steel (Fe-0.115C-20.9Mn-5.81Al-0.102V, all in wt pct) in the (a) RD-ND plane and (b) TD-ND plane. Straight features marked by red arrows in (b) are likely the boundaries of annealing twins in austenite grains.

Figure 6.10 shows an SEM image of the TD-ND plane of the microstructure of the high Mn duplex steel heat-treated for 1 h at 500 °C. In the SEM image of Figure 6.10, the brighter contrasted regions had a deeper nital etching response compared to the darker contrasted regions. Note that in the study by Xu et al. [6.12], who investigated similar duplex microstructures of a high Mn-Al steel (Fe-0.05C-26.0Mn-6.2Al, all in wt pct), the austenitic regions showed a deeper nital etching response compared to the ferritic areas. In the present study, the brighter contrasted regions contained straight features, likely annealing twin boundaries in austenite, similar to the as-received specimen microstructure in the LOM image (Figure 6.9(b)). It is interpreted based on these microstructural features (etching responses and straight features) that the regions with bright and dark contrast in the SEM image correspond to austenite and ferrite, respectively. Note that the “austenitic” regions often had an elliptical morphology (especially when viewed in the TD-ND plane) within the “δ-ferrite” network microstructures. It is acknowledged that the phases present in this sample have not been identified conclusively in this report, and the phase identification will be confirmed unambiguously through further experiments employing X-ray diffraction (XRD), electron backscatter diffraction (EBSD), and energy dispersive spectroscopy (EDS). Moreover, future examination will also analyze fine particles present in the ferrite regions (Figure 6.10), which may be related to precipitates like V carbides formed during aging heat treatment.
Figure 6.10  SEM micrograph of the high Mn duplex steel (Fe-0.115C-20.9Mn-5.81Al-0.102V, all in wt pct) heat treated for 1 h at 500 °C. The TD-ND plane of the microstructure is shown. The arrows indicate features likely corresponding to the boundaries of annealing twins in austenite grains.

Figure 6.11 shows LOM micrographs of the heat-treated microstructures (RD-ND plane) of the high Mn duplex steel. When heat-treated at 500 °C for 1 h, the microstructure consisted of elongated austenite and δ-ferrite regions, similar to the as-rolled microstructure. As the annealing temperature increased up to 900 °C, the overall austenite fraction increased compared to the microstructure annealed at 500 °C for 1 h. In addition, the ferrite band thickness generally became smaller with increasing annealing temperature to 900 °C. When heat-treated at the highest annealing temperature of 1100 °C, the elongated morphology started to diminish due to grain coarsening.

For the 1100 °C 1h annealing condition, the ferrite fraction appears to have increased compared to the samples annealed at a temperature of 700 and 900 °C, which is consistent with the thermodynamic calculations indicating that δ-ferrite is stabilized above 900 °C. It should be noted that the microstructural evolution as a function of the heat treatment condition was also analyzed in the TD-ND plane, which was generally similar to the trend of the RD-ND plane microstructure except that the elongated microstructures are more prominent in the RD-ND plane.

The Vickers hardness values for the high Mn duplex steel as a function of the analysis orientation and heat treatment conditions are shown in Figure 6.12. Note that the hardness was separately measured for the austenitic and ferritic regions, as shown in Figure 6.12. When tested in the RD-ND plane (Figure 6.12(a)), compared to the as-received condition, the average hardness of ferrite remained nearly constant (243-244 HV) after heat treating for 1 h at 500 and 600 °C. When the annealing temperature increased to 700 °C, the average hardness of ferrite increased to 256 HV. With increasing annealing temperature to 900 °C and 1100 °C, the ferrite hardness gradually decreased below 250 HV. Overall, the hardness results indicated that the highest hardness value for ferrite was achieved at an annealing temperature of 700 °C, which is possibly associated with a vanadium precipitation strengthening effect. Note that the thermodynamic calculation results in Figure 6.10(a) indicated that MC carbide is thermodynamically stable at/below 700 °C. As for austenite, the average hardness values ranged from 180 HV to 190 HV in the as-received condition and after annealing at temperatures of 500 and 700 °C. When heat-treated at 900 and 1100 °C, the austenite hardness values decreased to about 152-153 HV. In contrast to the ferrite, there was no increase in austenite hardness compared to the as-received condition possibly because MC carbide formation in austenite is limited due to the higher MC solubility. Interestingly, both ferrite and austenite hardness gradually
decreased with increasing annealing temperature above 700 °C, which may partly be associated with accelerated grain coarsening at higher temperatures. It is also possible that the hardness decreases at higher temperatures are partly related to the coarsening and/or dissolution of MC carbides in the ferritic regions.

Figure 6.11 shows the average Vickers hardness values obtained from the TD-ND plane. Overall trends for hardness in ferrite and austenite were similar to the RD-ND plane analyses. For the ferritic regions, the highest average hardness values (255 HV) were obtained from an intermediate range of the annealing temperatures (700 °C and 900 °C). It should be noted, however, that the ferrite hardness was relatively high in the as-received condition, different from the RD-ND plane analyses, which might be attributed to inhomogeneity in the microstructures. On
the other hand, austenite hardness generally decreased with increasing annealing temperature. The values averaged from hardness values of both ferritic and austenitic regions are also indicated with blue triangles in Figure 6.12. As expected, the overall average values were generally intermediate between those of ferritic and austenitic regions. The average hardness and standard deviation for all alloy conditions are summarized in Table 6.3.

![Figure 6.12](a) Average Vickers hardness values for austenite and ferrite in the microstructures of the high Mn duplex steel (Fe-0.115C-20.9Mn-5.81Al-0.102V, all in wt pct) as a function of heat treatment conditions. The hardness analysis was performed on polished samples on (a) the RD-ND plane and (b) the TD-ND plane. *(Color images – See PDF version)*

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Heat Treatment Conditions</th>
<th>Austenite (HV)</th>
<th>Ferrite (HV)</th>
<th>Average (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RD-ND</strong></td>
<td>As rolled</td>
<td>184 ± 4</td>
<td>244 ± 10</td>
<td>214 ± 32</td>
</tr>
<tr>
<td></td>
<td>500 °C, 1 h</td>
<td>181 ± 5</td>
<td>244 ± 3</td>
<td>213 ± 33</td>
</tr>
<tr>
<td></td>
<td>600 °C, 1 h</td>
<td>182 ± 2</td>
<td>243 ± 8</td>
<td>213 ± 32</td>
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<tr>
<td></td>
<td>700 °C, 1 h</td>
<td>185 ± 8</td>
<td>256 ± 6</td>
<td>220 ± 38</td>
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<td></td>
<td>900 °C, 1 h</td>
<td>153 ± 3</td>
<td>248 ± 12</td>
<td>201 ± 50</td>
</tr>
<tr>
<td></td>
<td>1100 °C, 1h</td>
<td>152 ± 5</td>
<td>233 ± 5</td>
<td>193 ± 43</td>
</tr>
<tr>
<td><strong>TD-ND</strong></td>
<td>As rolled</td>
<td>184 ± 11</td>
<td>255 ± 8</td>
<td>219 ± 39</td>
</tr>
<tr>
<td></td>
<td>500 °C, 1 h</td>
<td>185 ± 4</td>
<td>235 ± 4</td>
<td>210 ± 26</td>
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<tr>
<td></td>
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<td></td>
<td>700 °C, 1 h</td>
<td>173 ± 8</td>
<td>250 ± 5</td>
<td>211 ± 41</td>
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<td></td>
<td>900 °C, 1 h</td>
<td>158 ± 8</td>
<td>250 ± 10</td>
<td>204 ± 48</td>
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<tr>
<td></td>
<td>1100 °C, 1h</td>
<td>155 ± 6</td>
<td>242 ± 8</td>
<td>197 ± 47</td>
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### 6.5.3 Tensile Properties of Hot-Rolled High Mn Duplex Steel

Figure 6.13 shows the engineering stress-strain curves for the as-hot rolled high Mn duplex steel
specimens, tested in two different (RD//tensile axis and TD//tensile axis) orientations. When the specimen was
tensile tested along the TD, both yield strength and ultimate tensile strength were higher than those values along the
RD. Tensile test results are summarized in Table 6.4. The yield strength values evaluated from both orientations
(456-476 MPa) were within the target strength levels between 400-800 MPa for the DOE H2@Scale Program.

![Figure 6.13](image)

**Figure 6.13** Engineering stress-strain curves for the hot-rolled high Mn duplex steel in RD and TD.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Elongation (pct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile axis//RD</td>
<td>456</td>
<td>600</td>
<td>34</td>
</tr>
<tr>
<td>Tensile axis//TD</td>
<td>476</td>
<td>620</td>
<td>33</td>
</tr>
</tbody>
</table>

**Table 6.4 – Summary of Tensile Test Results for the As-Rolled High Mn Duplex Steel.**

6.5.4 Fractographs of Tested Duplex Stainless Steel Specimens

Figure 6.14 shows fractographs of the small CNT specimen of the 255 duplex stainless steel fractured in
the gaseous H environment (103 MPa H pressure). Note that this specimen was provided by SNL and analyzed
using an SEM available at Mines. A comparison of overall fractographic appearance between the gaseous H charged
specimen and small CNT specimen charged in NaOH aqueous solution was presented in the previous report [6.3],
but more detailed fractographic analyses were performed on the same specimens at this time. For the sample tested
in the gaseous H environment (Figure 6.14(a)), the ductile fracture region was observed away from the center of the
fracture surface of the small CNT specimen. This location of the ductile fracture zone is clearly different from the
small CNT specimen tested in the electrochemical charging condition, which showed a more symmetrical fracture
appearance with a ductile fracture region noted near the center of the fracture surface as reported previously [6.3].
On the other hand, the fracture appearance within the H-affected brittle fracture zone was generally similar between
the gaseous and electrochemical charging conditions [6.3]; the brittle fracture zone usually involved transgranular
(cleavage) fracture features as shown in Figure 6.15(c). Figure 6.14(d) highlights a large secondary crack that
formed near the brittle-to-ductile transition region, which was *not* noted in the small CNT specimen tested using
electrochemical charging [6.3].
Figure 6.14 SEM fractographs of the small CNT specimen of the 255 duplex stainless steel tested in gaseous H (103 MPa). (a) Overview SEM image indicating regions for (b), (c), and (d). (b) Ductile fracture region, corresponding to the area labeled b in (a). (c) Brittle fracture zone, corresponding to the area labeled c in (a). (d) Ductile-to-brittle transition region including a large crack near the center of the specimen, corresponding to the area labeled d in (a).

Figure 6.15 shows SEM fractographs of the CNT specimen fractured in air after being pre-charged at elevated temperature in the gaseous H environment. This specimen was also provided by SNL and analyzed at Mines. In contrast to the specimens tested in situ in the gaseous and electrochemical charging environments, the H pre-charged CNT specimen exhibited a ductile fracture region near the notch root (or specimen surface), as shown in Figure 6.15(a). Figure 6.15(b)-(c) show the ductile and brittle fraction regions, produced in the pre-charged condition. The fracture features within these two regions were generally similar to the specimens obtained from the in situ testing in the H charging environments. On the other hand, the thermally pre-charged condition showed a large area fraction that exhibits a mixed fracture mode consisting of both ductile and brittle fracture features (Figure 6.15(d)). The primary difference between the pre-charged condition and the in situ tested specimens is likely the H distribution during the testing. That is, before or during testing of the pre-charged sample in air, some of the H atoms may escape from the specimen, and the H desorption rate should in theory be much faster for ferritic regions than for austenitic regions. It is therefore possible that during the testing, the pre-charged condition was subject to a less homogeneous distributions of H within its microstructure as compared to the in situ tested specimens. The nonuniform H distribution in the pre-charged condition might have contributed to the wider area of the mixed-mode fracture region.
Figure 6.15  SEM fractographs of the CNT specimen of the duplex stainless steel, tested in air after thermal pre-charging in gaseous H environment. (a) Overview SEM image. (b) Ductile fracture region, corresponding to the area labeled b in (a). (c) Brittle fracture region, corresponding to the area labeled c in (a). (d) Region showing both ductile and brittle fracture features, corresponding to the area labeled d in (a).

Figure 6.16 shows SEM fractographs of the large CNT specimen after the HE tests with electrochemical charging using a 0.05 M NaOH solution with a current density of 1.65 mA cm$^{-2}$. Note that this charging condition resulted in a notch tensile strength (NTS) value of 929 MPa, closest to those obtained for the specimens tested in gaseous H (905-914 MPa) and the H pre-charged specimen (927 MPa). Overall, the fracture surface appearance for this large CNT specimen (Figure 6.16) was similar to that for the small CNT specimen tested in the equivalent charging condition (i.e., 0.05 M NaOH solution and 1.65 mA cm$^{-2}$ current density) [6.3]. For example, a micropore coalescence fracture appearance was evident in the central region of the fracture surface of the large CNT specimen (Figure 6.16(a) and (b)). In addition, a H-affected brittle fracture zone is clearly visible in the region surrounding the central ductile fracture zone (Figure 6.16(a) and (c)). The H-affected zone consisted of transgranular fracture features involving river patterns on cleavage facets in addition to H-induced secondary cracks. Moreover, a few circumferential cracks appeared near the notch root of the fracture surface (Figure 6.16(d)), which is similar to the behavior of small CNT specimens tested in the equivalent charging condition. In contrast, there were notable differences in the quantity and size of the H-induced cracks between the fractured large and small CNT specimens. In particular, the H-induced cracks in the large CNT specimen were generally larger than in the small CNT.
Figure 6.16(a), (e), and (f) show the morphology of several, large cracks that formed at the brittle to ductile fracture transition region of the fracture surface. The differences in the features of the transition region are likely a result of different notch geometries.

Figure 6.16  SEM fractographs of the large CNT specimen of the duplex stainless steel after in situ rising displacement testing in a 0.05 M NaOH aqueous solution under a current density of 1.65 mA cm$^{-2}$.  (a) Overview SEM image.  (b) Detailed image of the center region highlighting ductile fracture features.  (c) H-affected, brittle fracture region.  (d) Image taken near the specimen surface, i.e., region near the notch root.  (e) Image of macrocracks near the ductile to brittle transition region.  (f) Backscattered electron (BSE) image taken from the same region as (e).
6.6 Summary

Microstructure and microhardness of the high Mn duplex steel were analyzed in the as-rolled and heat-treated conditions. The microstructure evolution during the heat treatment was interpreted based on equilibrium phase fraction calculations and dilatometry results. Microhardness analysis results indicated that age-hardening (precipitation strengthening effect) was more pronounced in the ferritic regions compared to the austenitic regions. For ferritic regions, the peak-aged condition was noted at 700 °C. Tensile tests were performed on the as-rolled high Mn duplex steel. The yield strength values in the intercritically hot-rolled condition (1000 °C) were approximately 456-476 MPa, which are within the target strength level (400-800 MPa yield strength) pursued in the DOE H2@Scale program.

The fracture surfaces of the small and large CNT specimens tested in electrochemical charging conditions, the thermal H pre-charging condition, and in pressurized H gas were analyzed and compared. In general, the small and large CNT specimens tested in the equivalent charging conditions showed a similar fracture surface appearance, i.e., a central ductile fracture zone was surrounded by the H-affected brittle fracture zone. The small CNT specimen tested in pressurized H gas also showed two distinct (ductile and brittle) fracture zones, but the ductile fracture zone was located away from the center of the specimen. For the pre-charged specimen tested in air, mixed-mode fracture zones showing both cleavage facets and dimples were frequently observed, which was not the case for the other two specimens. These observations were interpreted in terms of the differences in H distribution within the microstructures during testing in air versus testing with in situ charging.

6.7 Research Plans for Next Reporting Period

The analysis of the evolution of the microstructure and hardness of the high Mn duplex steel as a function of heat treatment conditions will be continued to identify the heat treatment conditions with enhanced strength. For selected heat treatment conditions, tensile testing and HE testing will be performed to demonstrate enhanced combinations of strength and HE resistance for this steel. Using the remaining ingots of the high Mn duplex steel at U.S. Steel, potential microstructural alternations will be explored by tuning the rolling parameters, which influence the phase fractions/morphology and stored strain energy. In regard to the development of the accelerated HE testing method, H concentrations in the 255 duplex stainless steel samples will be measured for different H charging conditions. For both the high Mn duplex steel and duplex stainless steel, tensile testing with in situ neutron diffraction measurement was initiated at Los Alamos Neutron Science Center (LANSCE) to study the role of H on deformation mechanisms of these steels. The results of the neutron measurements will be presented in the next reporting period.

6.8 References


