Evaluation of the Susceptibility of Duplex Stainless Steel 2205 to Hydrogen Assisted Cracking in REAC Systems

Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

By

Mei He, B.S.
Graduate Program in Welding Engineering

The Ohio State University
2016

Thesis Committee:
Boian T. Alexandrov, PhD, Advisor
John C. Lippold, PhD, Co-Advisor
Abstract

Approximately ten years ago, carbon steel was replaced by duplex stainless steel (DSS) to fabricate the reactor effluent air cooler (REAC) of hydrocracker units in order to improve the performance and service lifetime of these units. Unfortunately, several catastrophic failures from around the world have been reported in REAC units constructed of DSS, most within five years of service. Based on failure analysis reports, the failures were generally associated with welded joints and were caused by crevice/pitting corrosion and stress corrosion cracking. Given the condition of hydrogen-rich environment, high-pressure process fluid, and service temperature, this type of cracking is most likely a form of hydrogen assisted cracking (HAC). It is highly influenced by phase balance (ferrite/austenite) after welding and welding procedures, with high levels of ferrite in the weld metal or HAZ increasing the susceptibility to HAC.

In this study, different weld metal phase balances were prepared by autogenous gas tungsten arc welding (GTAW) for using different welding parameters and shielding gases. The delayed hydrogen cracking test (DHCT) was used to evaluate the effects of the weld phase balance on the susceptibility to HAC in DSS 2205 welds. Using this approach, weld metal ferrite levels on the order of 90 vol% ferrite led to very rapid failure, while reducing the ferrite level to approximately 50-60 vol% greatly
increased resistance to HAC. Fractography was performed using a scanning electron microscope (SEM) and showed that brittle fracture morphologies occurred in the higher ferrite pass of overlapping two pass welds for each DHCT sample. A mixture of quasi-cleavage and intergranular fracture modes occurred during the crack nucleation and propagation process, and final sample failure was caused by overload exhibiting a microvoid coalescence fracture mode. The failure mechanism closely reproduced the actual service failures in REAC welds.

For different phase balances in HAZ, the HAZ samples were simulated over a range of cooling rates by Gleeble® 3800 system. It was found that the microstructure had significantly higher ferrite content with faster cooling rate controlled by different free span distances. The same approaches of DHCT and fractography to evaluate the susceptibility to HAC will be used for the simulated HAZ samples. The additional testing will be needed to examine the reproducibility of DHCT and to establish guidelines for the maximum ferrite content in 2205 weld metal and HAZ that will prevent service failures.

In summary, the DHCT exhibited high sensitivity and good reproducibility in determining the effect of weld metal ferrite content on HAC susceptibility in autogenous GTA welds of DSS 2205, and it can be an effective method to evaluate the effect of ferrite/austenite balance on the susceptibility to HAC in both the weld metal and HAZ.
Dedication

To my family, my boyfriend, and friends for their love and support.
Acknowledgements

I would like to thank to my advisors Boian Alexandrov and John Lippold for guidance, encouragement, and support during my two years of studies and life, and for being on my advising committee. Thanks to Shell Global Solutions for providing the funding and Dr. Jorge Penso for professional guidance and support for this research.

I would like to extend a special thank you to the Welding and Joining Metallurgy Group and all the past and present members of it, in particular Ken Copley, Ed Pfeifer, Dr. Desmond Bourgeois for their help with this project.
Vita

Sep, 2010 to May, 2014................................B.S. Material Science and Engineering

.................................................................The Ohio State University, Columbus, Ohio

2010 to Present ............................................Graduate Research Associate, Department of

Materials Science and Welding Engineering

.................................................................The Ohio State University, Columbus, Ohio

Publications

Aluminum to Copper and Stainless Steel by Vaporizing Foil Actuator: Effect of Heat
Treatment Cycles on Mechanical Properties and Microstructure." Metallurgical and

Field of Study

Major Field: Welding Engineering
Table of Contents

Abstract .................................................................................................................................................. ii

Dedication ............................................................................................................................................... iv

Acknowledgements .............................................................................................................................. v

Vita .......................................................................................................................................................... vi

List of Figures ......................................................................................................................................... x

List of Tables .......................................................................................................................................... xiv

Chapter 1 Introduction .......................................................................................................................... 1

Chapter 2 Background .......................................................................................................................... 3

  2.1 Refining Systems ............................................................................................................................ 3
      2.1.1 Typical Hydroprocessing Units ............................................................................................... 3
      2.1.2 REAC Systems ............................................................................................................................ 7
      2.1.3 Material Selection and Failure Cases of REAC Systems .............................................................. 7

  2.2 Duplex Stainless Steels ................................................................................................................... 11
      2.2.1 Introduction and History .......................................................................................................... 11
      2.2.2 Metallurgy of DSS .................................................................................................................... 15
      2.2.3 Weldability of DSS .................................................................................................................... 19

  2.3 Hydrogen Assisted Cracking ........................................................................................................... 23
      2.3.1 Hydrogen Cracking Theory ..................................................................................................... 23
List of Figures

Figure 2.1 Simplified Scheme of Refinery Process ......................................................... 4

Figure 2.2 Hydrotreating Unit Process Flow Diagram ..................................................... 5

Figure 2.3 Hydrocracking Unit Process Flow Diagram .................................................. 6

Figure 2.4 Yield Strength and PREN of Duplex and Austenitic Stainless Steels .................. 13

Figure 2.5 WRC-1992 .................................................................................................... 16

Figure 2.6 Pseudobinary phase diagram for duplex stainless steels ............................... 17

Figure 2.7 Example of sigma phase (arrows) .................................................................. 18

Figure 2.8 Isothermal precipitation diagram for DSS 2205 annealed at 1050°C ............... 19

Figure 2.9 Weld solidification cracking susceptibility versus Creq/Ni eq .......................... 21

Figure 2.10 Schematic of the decohesion theory .......................................................... 25

Figure 2.11 Interaction of hydrogen, microstructure, and tensile restraint to promote HIC .................................................................................................................. 27

Figure 2.12 Beachem’s diagram that predicts failure modes based on hydrogen concentration at crack tip and stress intensity factor ....... 27
Figure 2.13 CTS test set-up ........................................................................................................ 30
Figure 2.14 Schematic illustration of Tekken test ................................................................. 31
Figure 2.15 Schematic illustration of the implant test ......................................................... 33
Figure 2.16 Schematic illustration of the TRC test .............................................................. 34
Figure 2.17 Schematic illustration of the augmented strain cracking test ............ 35
Figure 4.1 DSS 2205 base metal microstructure with approximately 50% ferrite and 50% austenite. The austenite is the lighter etching phase ........................................................................................................ 39
Figure 4.2 WRC-1992 Diagram with Cr(eq) and Ni(eq) lines of DSS 2205 ........ 40
Figure 4.3 Mock-up samples (Top: header box mock-up, Bottom: header box mock-up together with tube-to-tubesheet mock-up) ................................................. 42
Figure 4.4 Design of header box mock-up .......................................................................... 43
Figure 4.5 Design of tube-to-tubesheet mock-up ............................................................... 44
Figure 4.6 Plate design and welding parameters of autogenous GTAW samples ........................................................................................................................................... 46
Figure 4.7 DHCT sample sketch after autogenous GTAW on top and bottom surfaces .......................................................................................................................... 48
Figure 4.8 DHCT sample after autogenous GTAW on top and bottom surfaces ......................................................................................................................... 48

Figure 4.9 Gleeble simulated sample set up ................................................................. 50

Figure 4.10 Thermal histories of HAZ simulated samples, DSS 2205 ............... 51

Figure 4.11 DHCT frame with the 10:1 lever arm ......................................................... 53

Figure 4.12 DHCT set-up .................................................................................................. 54

Figure 4.13 WM and HAZ optical images locations .................................................... 58

Figure 5.1 Ferrite content of Sample A in 2nd pass heat affected zone and weld metal ......................................................................................................................... 60

Figure 5.2 Ferrite content of Sample A, B, C, and D in 2nd pass weld metal ..... 62

Figure 5.3 Ferrite content of Sample E in 2nd pass (Left HAZ: 62%, Right WM: 54%) ............................................................................................................................... 63

Figure 5.4 Ferrite content image analysis of Sample A, B, C, and D in 2nd pass weld metal ......................................................................................................................... 64

Figure 5.5 Ferrite content of base metal and chosen HAZ simulated samples ................................................................................................................................. 67

Figure 5.6 Ferrite content Image Analysis of base metal and chosen HAZ simulated sample ......................................................................................................................... 68

Figure 5.7 DHCT results of Sample A, B, C, D, &E ...................................................... 71
Figure 5.8 Hydrogen assisted cracking failure in sample B ........................................... 73

Figure 5.9 Fracture surfaces of sample A & B sowing brittle quasi cleavage and intergranular morphology in the second pass weld and ductile micro-void coalescence morphology in the first pass weld................................. 74

Figure 5.10 Examples of intergranular, quasi cleavage (left), and microvoid coalescence (right) from the regions indicated in Sample A (Figure 5.8)........................................................................................................................................... 74

Figure A.1: DHCT Sample Design for Gleeble Samples ............................................. 84

Figure A.2: DHCT Sample Design for GTAW and Mock Up Samples ...................... 85

Figure A.3: DHCT Sample Machine Plan from Mock Up Sample ......................... 86

Figure B.1: Sample C ........................................................................................................ 87

Figure B.2: Sample D ........................................................................................................ 88
List of Tables

Table 2.1 Materials Compositions Used for REAC Systems (wt%) ............................ 8
Table 2.2 Reported 2205 DSS REAC Failure Cases.................................................. 10
Table 2.3 Common DSS Chemical Compositions ......................................................... 14
Table 2.4 Common DSS and 316L SS Mechanical Properties Comparison .............. 15
Table 4.1 Chemical composition of DSS 2205 steel and 26Cr-1Mo shim ................. 39
Table 4.2 Reported mechanical properties of purchased DSS 2205 ......................... 40
Table 4.3 Details of materials used in mock-up samples ............................................ 45
Table 4.4 Welding Parameters for Samples A, B, C, D, and E ................................. 47
Table 4.5 Gleeble simulated samples and base metal sample cooling rate and ferrite percentage .................................................................................................................. 52
Table 5.1 Weld Metal and HAZ Ferrite Content (ASTM 562-11) ............................ 65
Table 5.2 Gleeble simulated samples and base metal sample cooling rate and ferrite percentage .................................................................................................................. 66
Table 5.3 Weld Metal and HAZ Ferrite Content (ASTM 562-11) ............................ 70
Chapter 1 Introduction

In hydroprocessing units, the reactor effluent air cooler (REAC) is one of the most important pieces of equipment, which directly influences the whole high-pressure loop of flow. It is the final cooling solution before separating the vapor (recycle gas) from the oil effluent and the sour water. About 8 to 10 cases of Duplex Stainless Steels REAC failures have been reported around the world, in some cases leading to fire and explosion. The REAC is part of the hydrocracker unit, which is used to produce maximum distillates of high-speed diesel, kerosene, naphtha and liquefied petroleum gas (LPG). During the sulfur removal procedure, the reactions occur at high temperature with the presence of hydrogen. The process stream containing hydrogen sulfide (H₂S), ammonia (NH₃) and hydrogen chloride (HCl) after reactions enters REAC, which separates the hydrogen-rich vapor, hydrocarbon liquid, and water.

In most of the failure scenarios, cracking was located between either the top plate and tube sheet, or bottom plate and tube sheet of the header box. Metallurgical investigation of the failures revealed high ferrite content at the location of cracking, suggesting that the high ferrite levels in the weld metal and HAZ contribute to HAC. Fractographic analysis of these failures showed a mixture of ductile and brittle fracture modes.
Based on the assumption that HAC is the predominant failure mode and the presence of high ferrite levels at the failure locations, this study was designed to evaluate the relationship between ferrite content and HAC susceptibility in DSS 2205 welds. Samples with different phase balance (ferrite/austenite) were prepared using the GTAW process with different welding parameters and shielding gases and Gleeble simulation with different cooling rates. The delayed hydrogen cracking test (DHCT) was then used to evaluate the susceptibility to HAC. The sample during DHCT is loaded with a constant tensile stress (90% yield strength) and simultaneously charged with hydrogen in a continuous circulation of PH 1.10-1.12 electrolyte. Metallurgical characterization and ferrite content measurement techniques were used to quantify the phase balance as a function of different welding conditions. Fractographic analysis was performed on failed DHCT samples to determine the fracture morphologies and failure mechanism.
Chapter 2 Background

2.1 Refining Systems

2.1.1 Typical Hydroprocessing Units
The refinery is an industrial process plant where crude oil is processed and refined into more useful products such as petroleum naphtha, gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas.\textsuperscript{1} It is mostly considered as an essential part of the downstream side of the petroleum industry. During the hydrotreating process, the crude oil is separated and purified into fractions by fractional distillation after being heated in a furnace. From the lower boiling points to higher boiling points, Butane, Propane, petrol, kerosene, diesel, and fuel oil are separated out.\textsuperscript{1} The heavy bottom fractions often need to be cracked into lighter products before use. Hydrocracking is one of the methods to reprocess and upgrade the quality of the feedstock by using hydrogen at elevated temperature and pressures along with a suitable catalyst.\textsuperscript{2,3} A simplified scheme of a refinery process is illustrated in Figure 2.1.
It is very important to remove elements of sulfur and nitrogen during hydrotreating procedure. Sulfur can contaminate the catalyst, and nitrogen can degrade the product quality. Commonly after the reactions of hydrogen with sulfur and nitrogen
in hydroprocessing units, \( \text{H}_2\text{S} \) and \( \text{NH}_3 \) are produced in the hydrocarbon feed.\(^2\)

Figure 2.2 shows a typical hydrotreating process flow diagram.

![Hydrotreating Unit Process Flow Diagram](image1.png)

**Figure 2.2: Hydrotreating Unit Process Flow Diagram\(^2\)**

Hydrocracking is the process for low value hydrocarbon feedstock to crack and break down into higher value hydrocarbons. It typically takes heavy hydrocarbons to produce lighter hydrocarbons, such as cracking coke distillate to make gasoline.\(^2, 3\)

Figure 2.3 shows a typical hydrocracking process flow diagram.
Hydrocracking and hydrotreating units have very similar process flows. The feed is heated through exchangers and a furnace to reach the temperature of at least 700°F (370°C). Hydrogen is injected into the feed upstream of the reactor, and reacts with the catalyst that promotes reactions of hydrogen with sulfur and nitrogen together with feedstock to produce H₂S and NH₃. The reactor effluent is a mixture of hydrogen, hydrocarbons, H₂S, NH₃, and possibly HCl and H₂O. At downstream, the effluent is just cooled through a series of shell-and-tube heat exchangers. The injection of wash water into the reactor effluent stream is normally used to prevent fouling by NH₄HS and NH₄Cl salts, which are seen in upstream of the REAC or shell and tube heat exchanger. The water washed effluent enters separator vessel to separate the gas, liquid hydrocarbon, and sour water. The separator sour water includes inorganic salt, gas phase hydrogen and light hydrocarbon, and H₂S.
2.1.2 REAC Systems

In hydroprocessing units, units, the reactor effluent air cooler (REAC) is one of the most important pieces of equipment, which directly influence the whole high-pressure loop of flow.\(^5\) REAC is the final cooling solution before separating the vapor (recycle gas) from the oil effluent and the sour water.\(^2,5\) The outlet temperature directly impacts recycle gas molecular weight as larger hydrocarbon molecules drop out of the vapor phase.\(^5\) It also influences the hydrogen partial pressure and directly affects reactor catalyst life.\(^5\) However, the operation condition of high pressure and low temperature bring a lot of problems to REAC systems, such as NH\(_4\)HS and NH\(_4\)Cl precipitation which lead to pressure drop build-up, corrosion and or erosion-corrosion. At least 8-10 cases of welds failures have led to severe fire and explosion with loss of both time and money.\(^6-8\)

2.1.3 Material Selection and Failure Cases of REAC Systems

Older REAC designs mostly used carbon steels. As feeds in most heavy oil hydroprocessing service have more contents of sulphur and nitrogen, the concentrations of ammonium bisulphide with economic levels of water injection have risen to a point where carbon steel tubes have been substituted by alloy tubing and other materials.\(^5\) Currently materials used in REAC systems include carbon steel, Type 400 series stainless steels, Type 300 series stainless steels, Duplex Alloy 3RE60 and 2205, Alloy 800, Alloy825, and Alloy C-276.\(^2\) Table 2.1 shows the compositions of alloy used for REAC systems.
Carbon steel is a standard choice for colder portions of the effluent system for piping and pressure vessels, and for air coolers under low severity $\text{NH}_4\text{HS}$ conditions. After sour crudes became available, the concentration of $\text{NH}_4\text{HS}$ was increased to 3-8%. For carbon steels, it was expensive to inject polysulphide to continue using carbon steels. Especially, carbon steels are very susceptible to corrosion by $\text{NH}_4\text{HS}$ and wet $\text{NH}_4\text{Cl}$, hydrogen blistering, hydrogen induced cracking, and sulfide stress cracking. With the increasing demand of sour feeds, more corrosion resistant materials such as nickel-based alloys 625, 800, and 825 and duplex stainless steel 2205 that can handle up to 15% $\text{NH}_4\text{HS}$ were used. Along with nickel-based alloys’ great corrosion resistance, they are usually more expensive. Economically speaking, duplex stainless steel is a more practical alternative.
alternative with comparable protection against corrosion.

Duplex stainless steels are commonly used in these systems because of their advantages from both the ferritic and austenitic stainless steel families. They are very cost-effective for such high strength and reduced alloy element contents. The proper heat treatment, fabrication, and welding techniques have to be applied to maintain the balanced microstructure. During early stage of duplex REAC systems upgrading, some failed to show significant reliability improvements. There were several issues with fabrication techniques such as rapid cooling rate associated with thick header boxes resulting in high ferrite and poor corrosion resistance. There were also failures related to hydrogen embrittlement cracking or sulphide stress cracking (SCC). The weld procedures and practices API TR 938C were developed to minimize the microstructural deterioration during fabrication and to achieve good corrosion resistance in duplex stainless steels. Issues with duplex REAC systems have been one of the top topics in refinery industry for decades, and people have been dedicated to collect information for surveys. Table 2.2 below is the summary of public reported DSS REAC failure cases.
Table 2.2: Reported 2205 DSS REAC Failure Cases 6-8

<table>
<thead>
<tr>
<th>Case Number</th>
<th>Date</th>
<th>Details of Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2002</td>
<td>Sulfide stress cracking or hydrogen embrittlement of multiple tube-to-tubesheet welds shortly after start-up. Some welds were confirmed to have high ferrite.</td>
</tr>
<tr>
<td>2</td>
<td>11/2003</td>
<td>Cracked pipe weld at REAC outlet-cracking within the weld deposit. Weld hardness and ferrite met requirement. About 1.25 inch of pipe spring back at failure.</td>
</tr>
<tr>
<td>3</td>
<td>3/2005</td>
<td>32-inch long fracture with 37.5-inch total crack length in a header box weld resulting in an explosion and fire. Cracking occurred along the weld fusion line. Some evidence of high ferrite and high hardness found in weld deposit and HAZ.</td>
</tr>
<tr>
<td>4</td>
<td>6/2006</td>
<td>Multiple REAC outlet header and outlet piping weld cracks, some within weld deposits and some along weld fusion line. High ferrite identified at weld internal surfaces.</td>
</tr>
<tr>
<td>5</td>
<td>10/2009</td>
<td>Header box leaked during hydrotest following repairs to cracked tube-to-tubesheet welds. Cracked along weld fusion line. High ferrite in HAZ was found.</td>
</tr>
<tr>
<td>6</td>
<td>9/2010</td>
<td>Leak in pipe to nozzle weld at REAC outlet. Crack occurred along weld fusion line with some areas of high ferrite identified.</td>
</tr>
<tr>
<td>7</td>
<td>3/2012</td>
<td>Multiple tube-to-tubesheet leaks during hydrotest after cleaning a turnaround. REAC was built in 2004 following API TR 938-C guidelines.</td>
</tr>
<tr>
<td>8</td>
<td>2014</td>
<td>Header box welds failed after 2.5 years of service, leading to a significant fire. Plate materials confirmed to meet UNS32205. Failure attributed to weld root porosity, weld root corrosion and brittle fusion line fracture.</td>
</tr>
</tbody>
</table>
2.2 Duplex Stainless Steels

2.2.1 Introduction and History
Duplex stainless steels are combining good corrosion resistance with high toughness and mechanical strength, which are widely used in the chemical and petrochemical industries. They are significantly stronger and harder, and also have better chloride stress corrosion cracking resistance than the austenitic stainless steels. Even with good toughness and ductility, duplex stainless steels still have ductile-to-brittle transition at low temperature because of the high ferrite content. It limits the service temperature of duplex stainless steels to around -40 to 280°C. DSS typically have an annealed structure that is almost 50% ferrite and 50% austenite, although the ratios can vary from 35%/65%-55%/45%. DSS have existed since the 1930s. The name was from having equal proportions of austenite and ferrite. Back in around 1930, Uranus 50 was used after World War II for the heat exchanger tubing in nitric acid service. 3RE60 was then developed to improve the resistance to chloride stress corrosion. Years later, both wrought and cast duplex stainless steels have been used in more industry applications.

The first generation of duplex stainless steels such as Type 329 (UNS S32900) had good performance characteristics but had unacceptable corrosion resistance and toughness in the as-welded condition. The heat affected zone (HAZ) of welds had low toughness because of excessive ferrite, and significantly lower corrosion resistance than that of the base metal. During the upgrading process of argon oxygen decarburization (AOD), addition of nitrogen alloying of duplex stainless
steels makes possible for new stainless steels to increase HAZ toughness and corrosion resistance approaching that of the base metal in the as-welded condition. With increased austenite stability, nitrogen also reduces the rate at which undesired intermetallic phases form.\(^9\)

The second-generation duplex stainless steels are defined by their nitrogen alloying. In the late 1970s, offshore gas and oil fields in the North Sea directly influenced the demand for stainless steels with excellent chloride corrosion resistance, good fabricability, and high strength.\(^6\) Duplex stainless steel 2205 became very popular among the second generation duplex stainless steels and was widely used for gas gathering line pipe and process applications on offshore platforms.\(^6\) The high strength of these steels made it possible to reduce wall thickness and to reduce weight on the platforms.\(^9\)

In the similar way of dividing grades for austenite stainless steels, the duplex stainless steels are divided into different groups and grades according to their corrosion performance depending on the alloy content: lean duplex stainless steels (2101, 2003), conventional duplex stainless steels (2205), super duplex stainless steels (2507), and hyper duplex stainless steels (2707, 3207).\(^11\)

In refinery industry, DSS are used when austenitic stainless steels have problems with chloride pitting or chloride stress corrosion cracking (CSCC). The primary elements that contribute to the pitting corrosion resistance are Cr, Mo, and N. W, although not commonly used, is about half as effective on a weight percent basis as
Mo. Pitting resistance equivalent number (PREN) was developed to relate a stainless steel's composition to its relative pitting resistance in chloride containing solutions. The PREN relationship for austenite and duplex stainless steels is given as: \[ \text{PREN} = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + 16\text{N}. \]

Where Cr, Mo, W, and N represent the chromium, molybdenum, tungsten, and nitrogen contents of the alloy in weight percentage. Figure 2.4 shows a comparison of some DSS with various austenitic stainless steels with the differences in yield strength and chloride corrosion resistance (PREN).

Figure 2.4: Yield Strength and PREN of Duplex and Austenitic Stainless Steels
From Figure 2.4, DSS obviously shows better combinations of higher yield strength and corrosion resistance. For common DSS, the chemical compositions are listed in Table 2.3 as below, and also the mechanical properties of common DSS and austenitic SS for comparison in Table 2.4.

Table 2.3: Common DSS Chemical Compositions\textsuperscript{10}

<table>
<thead>
<tr>
<th>UNS Number</th>
<th>Type \textsuperscript{b}</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>N</th>
<th>Cu</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Min Pitting \textsuperscript{e}</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>S32000</td>
<td>Type 329</td>
<td>22.0 to 26.0</td>
<td>1.0 to 2.0</td>
<td>2.5 to 5.0</td>
<td>—</td>
<td>—</td>
<td>0.080</td>
<td>1.00</td>
<td>0.040</td>
<td>0.030</td>
<td>0.030</td>
<td>0.75</td>
<td>26.3</td>
</tr>
<tr>
<td>S31500</td>
<td>&quot;3RE60&quot;</td>
<td>16.0 to 19.0</td>
<td>2.5 to 3.0</td>
<td>4.25 to 5.25</td>
<td>0.05 to 0.10</td>
<td>—</td>
<td>0.030</td>
<td>1.20 to 2.00</td>
<td>0.030</td>
<td>0.030</td>
<td>1.40 to 2.00</td>
<td>27.1</td>
<td>—</td>
</tr>
</tbody>
</table>

Lean and Semi-lean DSS

<table>
<thead>
<tr>
<th>UNS Number</th>
<th>Type \textsuperscript{b}</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>N</th>
<th>Cu</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Min Pitting \textsuperscript{e}</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>S32304</td>
<td>2304 \textsuperscript{d}</td>
<td>21.5 to 24.5</td>
<td>0.05 to 0.60</td>
<td>3.0 to 5.5</td>
<td>0.05 to 0.20</td>
<td>0.05 to 0.60</td>
<td>0.030</td>
<td>2.50</td>
<td>0.040</td>
<td>0.030</td>
<td>1.00</td>
<td>22.5</td>
<td>—</td>
</tr>
<tr>
<td>S32101</td>
<td>2101</td>
<td>21.0 to 22.0</td>
<td>0.10 to 0.80</td>
<td>1.3 to 1.7</td>
<td>0.20 to 0.25</td>
<td>0.10 to 0.80</td>
<td>0.040</td>
<td>4.0 to 6.0</td>
<td>0.040</td>
<td>0.030</td>
<td>1.00</td>
<td>24.5</td>
<td>—</td>
</tr>
<tr>
<td>S32003</td>
<td>2003</td>
<td>18.5 to 22.5</td>
<td>1.5 to 2.00</td>
<td>3.0 to 4.0</td>
<td>0.14 to 0.20</td>
<td>—</td>
<td>0.030</td>
<td>2.00</td>
<td>0.030</td>
<td>0.020</td>
<td>1.00</td>
<td>26.7</td>
<td>—</td>
</tr>
</tbody>
</table>

Standard DSS

<table>
<thead>
<tr>
<th>UNS Number</th>
<th>Type \textsuperscript{b}</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>N</th>
<th>Cu</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Min Pitting \textsuperscript{e}</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>S31603</td>
<td>—</td>
<td>21.0 to 23.0</td>
<td>2.5 to 3.5</td>
<td>4.5 to 6.5</td>
<td>0.08 to 0.20</td>
<td>—</td>
<td>0.030</td>
<td>2.00</td>
<td>0.030</td>
<td>0.020</td>
<td>1.00</td>
<td>30.5</td>
<td>—</td>
</tr>
<tr>
<td>S32205</td>
<td>2205 \textsuperscript{d}</td>
<td>22.0 to 23.0</td>
<td>3.0 to 3.5</td>
<td>4.5 to 6.5</td>
<td>0.14 to 0.20</td>
<td>—</td>
<td>0.030</td>
<td>2.00</td>
<td>0.030</td>
<td>0.020</td>
<td>1.00</td>
<td>34.1</td>
<td>—</td>
</tr>
</tbody>
</table>

25 % Cr and Super DSS

<table>
<thead>
<tr>
<th>UNS Number</th>
<th>Type \textsuperscript{b}</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>N</th>
<th>Cu</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Min Pitting \textsuperscript{e}</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>S31200</td>
<td>—</td>
<td>24.0 to 26.0</td>
<td>1.2 to 2.0</td>
<td>5.5 to 6.5</td>
<td>0.14 to 0.20</td>
<td>—</td>
<td>0.030</td>
<td>2.00</td>
<td>0.045</td>
<td>0.030</td>
<td>1.00</td>
<td>30.2</td>
<td>—</td>
</tr>
<tr>
<td>S31280</td>
<td>—</td>
<td>24.0 to 26.0</td>
<td>2.5 to 3.5</td>
<td>5.5 to 7.5</td>
<td>0.10 to 0.30</td>
<td>0.20 to 0.80</td>
<td>0.030</td>
<td>1.00</td>
<td>0.030</td>
<td>0.030</td>
<td>0.75</td>
<td>34.0</td>
<td>W: 6.1 to 0.5</td>
</tr>
<tr>
<td>S32500</td>
<td>—</td>
<td>24.0 to 26.0</td>
<td>3.0 to 5.0</td>
<td>5.5 to 8.0</td>
<td>0.20 to 0.35</td>
<td>0.50 to 3.00</td>
<td>0.030</td>
<td>1.50</td>
<td>0.035</td>
<td>0.020</td>
<td>0.80</td>
<td>37.1</td>
<td>—</td>
</tr>
<tr>
<td>S32900</td>
<td>2540 \textsuperscript{d}</td>
<td>24.0 to 27.0</td>
<td>2.9 to 3.9</td>
<td>4.5 to 6.5</td>
<td>0.10 to 0.25</td>
<td>1.50 to 2.50</td>
<td>0.040</td>
<td>1.50</td>
<td>0.040</td>
<td>0.030</td>
<td>1.00</td>
<td>35.2</td>
<td>—</td>
</tr>
<tr>
<td>S32750</td>
<td>2507 \textsuperscript{d}</td>
<td>24.0 to 26.0</td>
<td>3.0 to 5.0</td>
<td>6.0 to 8.0</td>
<td>0.24 to 0.32</td>
<td>0.50</td>
<td>0.030</td>
<td>1.20</td>
<td>0.035</td>
<td>0.020</td>
<td>0.80</td>
<td>37.7</td>
<td>—</td>
</tr>
<tr>
<td>S32760</td>
<td>Z100</td>
<td>24.0 to 26.0</td>
<td>3.0 to 4.0</td>
<td>6.0 to 8.0</td>
<td>0.20 to 0.30</td>
<td>0.50 to 1.00</td>
<td>0.030</td>
<td>1.00</td>
<td>0.030</td>
<td>0.010</td>
<td>1.00</td>
<td>37.9 \textsuperscript{d}</td>
<td>W: 6.5 to 1.0</td>
</tr>
</tbody>
</table>
2.2.2 Metallurgy of DSS

DSS solidify from a fully ferritic microstructure to partially transform to austenite within the ferritic microstructure depending on alloy composition with further cooling. When rapid cooling from the solution annealing temperature, the final microstructure can end up with roughly 50% austenite and 50% ferrite at room temperature. With the addition of Nitrogen, it promotes austenite formation from ferrite at higher temperature and allows the desired phase balance to develop faster and quicker during initial solidification.11

Solidification of DSS is very composition dependent. Minor changes in composition can have a significant effect on the relative volume fraction of austenite and ferrite that is commonly illustrated as ferrite number (FN), as indicted in Figure 2.5 of WRC-1992 diagram with lines of FN. Every alloying element promotes either the formation of austenite or ferrite.8 The austenite/ferrite phase balance in the
microstructure can be predicted by Chromium equivalence ($Cr_{eq}$) and Nickel equivalence ($Ni_{eq}$). Their relationships with different alloying elements are listed as below:

$$Cr_{eq} = Cr + Mo + 0.7\ Nb$$

$$Ni_{eq} = Ni + 35\ C + 20\ N + 0.25\ Cu$$

Figure 2.5: WRC-1992

Pseudobinary phase diagram for duplex stainless steels as shown below in Figure 2.6 also can be a tool to understand the solidification process.
The goal of obtaining the desired phase balance is achieved primarily by adjusting alloying composition, and then by controlling the thermal history. Excessive ferrite can be caused by extremely low heat input welding or too fast quenching. Rapid quenching doesn’t leave enough time for transformation from ferrite to austenite to fully complete. For the welded structures, the heat input has to be optimized according to weld configuration so that the cooling rate will be quick enough to avoid detrimental phases but not so fast that ferrite content is too high close to the fusion line.\textsuperscript{9}
For desired phase balance without detrimental intermetallic phases, precipitates can form in a matter of minutes at the critical temperature. Intermetallic phases include complex compounds of iron, chromium, and molybdenum. They usually result from excessively high heat inputs or excessive cumulative time at high temperatures (700°C to 955°C) during welding and cooling after annealing.\textsuperscript{10,14} Figure 2.7 shows a microstructure of DSS 2205 aged at 850°C for 40 minutes then ended up with sigma phase precipitation on the grain boundaries of austenite and ferrite. Sigma phase can reduce corrosion resistance and toughness significantly. Figure 2.8 below is the isothermal precipitation diagram example for DSS 2205, annealed at 1050°C. Dash lines are sigma phase and nitride precipitation curves for DSS 2507 and DSS 2304 for the comparison purpose.\textsuperscript{13}

![Image of sigma phase](image)

**Figure 2.7: Example of sigma phase (arrows)**\textsuperscript{12}
All these precipitation reactions are time and temperature dependent. In order to limit the formation of intermetallic phases, limiting the time during the dangerous temperature range and low interpass temperature range can be effective. At the same time, the welding procedure, material thickness, and material grade all can make the limit variable.

### 2.2.3 Weldability of DSS

For weldability, it is the capacity of material to be welded under the imposed fabrication conditions into a specific, suitably designed structure and to perform satisfactorily in the intended service. Since welding is one of the most widely used
fabrication processes, it is required that engineering materials to be welded should possess good weldability. When welding DSS, two main possible problems are excessive ferrite content in the HAZ or weld deposit and the formation of detrimental intermetallic phases in the HAZ and weld deposit. These two main problems caused the failures such as weld solidification cracking, hydrogen induced cracking, intermediate-temperature embrittlement, sigma phase embrittlement, and etc.\textsuperscript{11}

DSS are known as being resistant to weld solidification cracking, even it can still happen. Some failures happened because of low impurity levels and small continuous liquid films along the grain boundaries.\textsuperscript{11} Weld solidification cracking is strongly dependent on the compositions. Figure 2.9 shows the weld solidification cracking susceptibility according to Cr\textsubscript{eq} and Ni\textsubscript{eq}. F mode of solidification can be the reason for presence of ferrite-ferrite grain boundaries that are easy to wet at the end of solidification and excessive ferrite content without sufficient transformation time from ferrite to austenite during cooling. The cracking resistance together with corrosion resistance in the HAZ and weld deposit can be improved with proper choice of filler metal.\textsuperscript{11}
Figure 2.9: Weld solidification cracking susceptibility versus $\frac{Cr_{eq}}{Ni_{eq}}^{11}$

Excessive ferrite content in the HAZ and weld deposit can also be a concern for hydrogen cracking as well, which is considered as DSS being resistant to. Hydrogen cracking can only happen under the combined condition of sufficient hydrogen, stress, and susceptible microstructure (high FN deposits).$^{15,16}$ Most failure cases have occurred because of high hydrogen contents and poor microstructure control.$^{11}$ For DSS used in refineries, the environment always involves a water phase containing $H_2S$ and $NH_3$ which is a risk of hydrogen cracking at welded locations such as root pass, mid-thickness, and cover pass.$^9,^{17}$ The most efficient way to avoid hydrogen cracking in DSS is to control the ferrite content in the HAZ and weld deposit. With a balanced ferrite/austenite microstructure, it can limit hydrogen
diffusion and prevent crack growth. Low hydrogen welding procedures are also recommended in moist environment for SMAW and SAW processes.\textsuperscript{11}

For the second problem of detrimental intermetallic phases in the HAZ and weld deposit, they are very harmful for ductility, toughness, and corrosion resistance. From Figure 2.8, sigma, chromium nitride, and alpha prime phases can precipitate depending on its different critical temperature range and cumulative time at that temperature range. The sigma phase formation in DSS is eutectoid type reaction of ferrite into sigma phase and austenite on slow cooling during range of 700°C - 1000°C.\textsuperscript{14} It nucleates at ferrite-austenite interface and grows inwards into the ferrite phase.\textsuperscript{18} The presence of sigma phase decreases the pitting resistance, toughness, and ductility to cause sigma phase embrittlement. With increasing molybdenum and chromium content, it is easier for sigma phase to precipitate. At 475°C embrittlement temperature range, alpha prime can form after extended exposure with increased hardness and decreased toughness. Any heat treatment in the critical temperature range for alpha prime formation of 300°C to 525°C has to be avoided in case of alpha prime embrittlement. That’s why it decides the upper temperature limit for DSS service.\textsuperscript{11} The focus of this study is DSS 2205’s hydrogen assisted cracking failure analysis and susceptibility evaluation.
2.3 Hydrogen Assisted Cracking

2.3.1 Hydrogen Cracking Theory
Hydrogen cracking can be divided into two types of hydrogen induced cracking and hydrogen assisted cracking depending on the source of hydrogen. Hydrogen from moisture, decomposition products of cellulose-type electrode, and contaminants on filler metal and weldments can enter the weld pool, then later on at ambient temperature it can cause a delayed cracking because of the hydrogen diffusion during the welding process. Hydrogen from environment together with the factor of stress can cause hydrogen assisted cracking during service and during welding.\textsuperscript{19, 20}

With decades of study on hydrogen cracking and many theories of hydrogen cracking or hydrogen embrittlement, there still isn’t one unified mechanism or theory to fully explain hydrogen cracking.\textsuperscript{19} Some past theories will be summarized later to have a better understanding of cracking phenomenon and mechanisms.

Planar pressure theory proposed by Zapffe and Sims states that the atomic hydrogen diffuses to internal defects like voids and forms molecular hydrogen that will increase the pressure after hydrogen is built up.\textsuperscript{22} The high internal hydrogen pressure can increase elastic strength of material and initiate a crack and then further enhance crack propagation to failure.

Surface adsorption theory was introduced by Petch and Staables after Zapffe. They disagreed on the planar pressure theory that increased pressure caused cleavage and transgranular fracture.\textsuperscript{23} They believed that the surface free energy of an atomically clean metal is lowered by hydrogen adsorbed onto the internal crack
surface, which allows brittle fracture to occur at lower stresses. With experimental support, the surface adsorption theory explains the effect of hydrogen in an iron lattice and the relationship between reduced surface energy and fracture stress.

Decohesion theory was proposed by Troiano in 1959 that the high triaxial stress concentration attracts dissolved hydrogen which further reduces the cohesive strength of the metallic lattice. Decohesion theory was proposed by Troiano in 1959 that the high triaxial stress concentration attracts dissolved hydrogen which further reduces the cohesive strength of the metallic lattice. Decohesion theory was proposed by Troiano in 1959 that the high triaxial stress concentration attracts dissolved hydrogen which further reduces the cohesive strength of the metallic lattice. Decohesion theory was proposed by Troiano in 1959 that the high triaxial stress concentration attracts dissolved hydrogen which further reduces the cohesive strength of the metallic lattice. Decohesion theory was proposed by Troiano in 1959 that the high triaxial stress concentration attracts dissolved hydrogen which further reduces the cohesive strength of the metallic lattice. The triaxial stress concentration exists at crack tip and attracts dissolved hydrogen. After it reaches the critical hydrogen concentration, a small crack forms and propagates into the region enriched with hydrogen. The crack propagation depends on the localized increasing hydrogen concentration in front of the crack, and can be shown schematically in Figure 2.10.
Hydrogen enhanced localized plasticity (HELP) theory was brought up by several researchers including Sofronis, Birnbaum, and Lynch. The HELP theory proposed that with the presence of hydrogen in solid solution the barriers to dislocation motion is decreased and the local plasticity increases. This fracture process doesn’t have characteristics of an embrittlement, but possibly a highly localized plastic failure process. The HELP model assumes that hydrogen solutes can act as shielding of the elastic interaction between obstacles and dislocations. The mobility of dislocation is enhanced by the reduction in the interaction energy between the
elastic stress centers, which causes inhomogeneous hydrogen distribution and low intrinsic material flow stress at higher hydrogen concentration position.

Beachem proposed a hydrogen cracking theory that turns away from the conventional hydrogen embrittlement approach and suggests a new mechanism of hydrogen assisted cracking (HAC). This stress intensity model describes the presence of a high hydrogen concentration at the crack tip can trigger any deformation mechanism that is happening in this region including intergranular, quasicleavage, and microvoid coalescence. These deformations are dependent on the microstructure, crack tip intensity, and the hydrogen concentration combined factors that can be illustrated in Figure 2.11.26 The model also states that instead of hydrogen locking dislocation in place, it unlocks the dislocation allowing hydrogen to move freely at lower stresses or multiply. Figure 2.12 below shows a diagram that can predict the failure mode based on stress intensity and hydrogen concentration at the crack tip.
Figure 2.11: Interaction of hydrogen, microstructure, and tensile restraint to promote HIC.\textsuperscript{19}

Figure 2.12: Beachem's diagram that predicts failure modes based on hydrogen concentration at crack tip and stress intensity factor\textsuperscript{19}
Whether it is hydrogen pressure build up, reduction in surface energy within the weld lattice, decohesion of microstructure, precipitation of a low ductility phase or hydrogen aiding different deformation mechanisms, it is clear that hydrogen has detrimental effects on materials that are exposed to hydrogen, whether internally from welding procedure or externally from service environment. With fundamental three conditions of tensile stress, susceptible microstructure, and threshold level of hydrogen all together, hydrogen cracking can happen.

Hydrogen cracking in steels can occur in both the weld metal and the HAZ, although it is most prevalent in the HAZ due to the combination of microstructure and tensile restraint that exists in this region of the weld. The composition and microstructure of the weld metal can usually be controlled to minimize or eliminate hydrogen cracking. For this study on DSS 2205’s hydrogen assisted cracking failures in refineries, the reason that most researchers believe is the susceptible microstructure of high FN in the HAZ and weld metal.

2.3.2 Experimental Methods for Evaluation of HAC Susceptibility

For hydrogen cracking tests, they can be divided into two groups: self-restraint tests and externally loaded tests. Self-restraint tests depend on the geometry and phase transformation properties of the specimen with stresses that are more representative of service conditions and are easy to apply. External loaded tests allow higher levels of restraint to be applied to a welded sample that induce high magnitudes of residual stresses.
Among the self-restraint tests, the controlled thermal severity (CTS) test, the Y-groove (or Tekken) test, and the gapped bead-on-plate (G-BOP) test are the most popular ones.

The specimens used for CTS test consist of one bottom plate and on top plate that is to be investigated. The top plate is bolted to the bottom plate and two anchor fillet welds to provide restraint as illustrated in Figure 2.13. Two test welds made under controlled conditions are deposited on opposite side, and then a tensile restraint is created in the fillet weld metal and HAZ of the top plate. With a machined notch in the top plate can provide stress concentration at the weld metal and HAZ interface and further promote crack initiation. With metallographic examination of root of the weld to determine if hydrogen cracking occurred or not is used to evaluate the susceptibility of weld metal and HAZ hydrogen cracking by the CTS test. However, later on it was found that the strain level used by the CTS test is lower than real welded structures.
Tekken test was developed by Kihara et al. In the test, low-hydrogen filler metal is used to deposit two restraining welds on each end of the weld groove prepared from the steel of interest. A single test is deposited later with filler metal to be investigated in the restrained assembly. Metallographic examination of specified locations of the test weld after no less than 72hrs. Test details and set up is illustrated in Figure 2.14.
The y-joint seen in Figure 2.14 induces high restraint in the root of the weld and is used to assess the susceptibility of HAZ hydrogen cracking. The vertical root slot causes less weld root restraint comparing to the y-joint and can be used to test the susceptibility of weld metal hydrogen cracking.\textsuperscript{20} The crack can either propagate in the weld metal or in the HAZ depending on the relative cracking susceptibility. Tekken test provides more restraint compared to CTS test because of the sample geometry design.
G-BOP test was introduced by Graville and McParlan in 1974. This test utilizes two ASTM A36 or CSA G40.21 steel blocks. One of the blocks is required to have a small ¾ mm machines recess, which produces high amounts of stress concentration in the test weld. Welds are performed across the top of the blocks and along the gap. After the welds are deposited on the blocks, they are clamped together for 24hrs then heated to a dull red color with a torch. Determining if there is hydrogen cracking or not depends on discoloration on the fracture.

The tests mentioned above are most common self-restraint tests. Among the externally loaded tests, the implant test, tensile restraint cracking (TRC) test, and augmented strain cracking test are most often used.

The implant test is used to investigate the hydrogen assisted cracking susceptibility of high strength steel base metal. The cylindrical sample with a circumferential notch and a screw thread is press fitted into a hole in the base plate. After the cylindrical sample in mounted into the base plate, a weld deposited along the base plate and the cylindrical sample. A tensile load then is added on the cylindrical sample and the motion is monitored for 24hrs. The susceptibility to hydrogen assisted cracking is quantified by the relationship between the applied stress and time to failure. The factors that can impact the hydrogen assisted cracking susceptibility include preheat, welding procedure, electrodes and welding parameters. Modifications to this test have been made to better place the circumferential notch in regions that include the HAZ so that the test can provide more reproducible results. Figure 2.15 below shows the implant test setup.
The TRC test was developed by Suzuki to study the hydrogen induced root cracking in butt weld joints. After the butt welding, a constant tensile load is added on the test weld until root cracking failure happens. The time for cracking to initiate and propagate is dependent on the tensile stress applied. The failure time will decrease with less tensile load. There is a critical stress level, crack will no occur below that. This critical stress level is used to rate the hydrogen induced cracking susceptibility. The test set up is shown in Figure 2.16 below.
Although with modification for the TRC test later on, the limitation is that the test is effective to evaluate the hydrogen cracking in the weld metal instead of the weld HAZ.

Augmented strain cracking test was introduced by Savage and etc in 1970s. The test was designed to produce hydrogen cracking and observe the initiation and propagation of cracks. After one pass of bead-on-plate welding, the test specimen was quenched right after to reduce hydrogen diffusion and minimize the loss of diffusible hydrogen. Then the specimen was placed in the augmented strain cracking test fixture with a loading apparatus. The loading apparatus provides...
constant stress and strain.\textsuperscript{34} The test set up is illustrated in Figure 2.17 below.

![Figure 2.17: Schematic illustration of the augmented strain cracking test\textsuperscript{19}](image)

The stress is provided by a four-point bending setup, and the strain is applied by using a die block pushing against the specimen. The relationship among applied strain, hydrogen content, microstructure and fracture behavior can be quantitatively assessed, and then the cracking susceptibility of the weld metal can be evaluated.\textsuperscript{19}

Different mechanisms and different testing methods of hydrogen cracking are included in this part because the testing method used to simulate actual service conditions and to rank susceptible components are similar to the Delayed Hydrogen Cracking Test (DHCT) method used in this study. It is important to understand
previous testing methods in order to apply various experimental designs to the DHCT and to evaluate testing results better.
Chapter 3 Research Objectives

Based on recent failures in REAC systems built using DSS 2205, it is necessary to better understand the failure mechanism and to determine the relationship between HAC susceptibility and the ferrite/austenite phase balance. Moreover, once the effect of microstructure is determined, other factors of HAC susceptibility such as welding process and weld joint geometry can be evaluated.

1) Evaluate the effect of the weld phase balance and microstructure on the susceptibility of DSS 2205 welds (weld metal and HAZ) to Hydrogen Assisted Cracking (HAC).

2) Validate the Delayed Hydrogen Cracking Test (DHCT) as a reliable method to determine the effect of weld metal/HAZ ferrite content on HAC susceptibility for DSS 2205 with high sensitivity and good reproducibility.

3) Provide recommendations on (1) selection of base metal compositions and (2) welding processes/parameters that will reduce the risk of HAC in DSS.
Chapter 4 Materials & Procedures

4.1 Materials

4.1.1 Base Metal

DSS 2205 (UNS-S32205) plate was used in this study for the production of all the autogenous GTAW samples and Gleeble simulated samples. The composition of the base metal is listed in Table 4.1 and the microstructure is shown in Figure 4.1. Reported mechanical properties from material provider are listed in Table 4.2.

Using the WRC-1992 diagram (Figure 4.2), the Cr(eq) is 25.86 and Ni(eq) is 9.5. The weld metal ferrite number estimation based on this composition is FN 98, which equates to a level of approximately 70 vol% ferrite. In order to increase the ferrite content of the weld metal above this level, a ferritic stainless steel (26Cr-1Mo) shim (Table 4.1) was used with autogenous GTAW to create a level of 90% ferrite content, as describe in the following section.
Table 4.1: Chemical composition of DSS 2205 steel and 26Cr-1Mo shim

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSS 2205 (Actual)</td>
<td>Cr   Ni   Mo  Mn  Cu  Co  Si  C  N  S</td>
</tr>
<tr>
<td></td>
<td>22.5  5.74 3.35 1.32 0.19 0.11 0.32 0.009 0.17 0.006</td>
</tr>
<tr>
<td>26Cr-1Mo Shim (Nominal)</td>
<td>26.0 0.15 1.0 0.05 0.02 0.002 0.20 0.01 0.01 0.01</td>
</tr>
</tbody>
</table>

Figure 4.1: DSS 2205 base metal microstructure with approximately 50% ferrite and 50% austenite (The austenite is the lighter etching phase)
Table 4.2 Reported mechanical properties of purchased plate of DSS 2205

<table>
<thead>
<tr>
<th></th>
<th>DSS 2205 (UNS-S32205)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness HV</td>
<td>222</td>
</tr>
<tr>
<td>Yield Strength (ksi)</td>
<td>80.5</td>
</tr>
<tr>
<td>Tensile Strength (ksi)</td>
<td>112.3</td>
</tr>
<tr>
<td>Bend</td>
<td>OK</td>
</tr>
<tr>
<td>Elongation % in 2”</td>
<td>40.4</td>
</tr>
<tr>
<td>Reduction of Area</td>
<td>69.1</td>
</tr>
</tbody>
</table>

Figure 4.2: WRC-1992 Diagram with Cr(eq) and Ni(eq) lines of DSS 2205
4.1.2 Mock-up Samples

According to project proposal, mock-up samples with GTAW and GMAW test welds will be supplied by sponsor. The welds should be produced with currently used welding procedures for metallurgical characterization and testing susceptibility. Unfortunately, the mock-up samples were delayed on the arrival time for a year and half. This thesis won’t include any testing results from the mock-up samples, but will be mentioned in the future work. Figure 4.3 below shows the mock-up samples of header box mock-up sample and tube-to-tubesheet mock-up sample.
Figure 4.3: Mock-up samples (Top: header box mock-up, Bottom: header box mock-up together with tube-to-tubesheet mock-up)
The detailed sample geometry and welding parameters are shown in Figure 4.4 and Figure 4.5, which were provided and made by Hudson Products Corporation located in Texas.

**Figure 4.4: Design of header box mock-up**
Figure 4.5: Design of tube-to-tubesheet mock-up

The good plate and bad plate mentioned in Figure 4.4 and Figure 4.5 are based on the Ni and N compositions of DSS 2205 plates used. The details of material used for the mock-up samples are explained in Table 4.3 also provided by Hudson Products Corporation.
The plan is to work on metallurgical examination and DHCT at different HAC susceptible locations of the samples, such as four corner welds for the header box mock-up sample.
4.2 Design of Autogenous Welded Samples

For further use with DHCT, plate of 12in length by 12in width with 0.5in thickness was machined to four 3 in. wide strips with a 1 in. x 0.2 in. gauge section, as shown in Figure 4.6. In this configuration, the welds were oriented parallel to the plate rolling direction.

![Figure 4.6: Plate design and welding parameters of autogenous GTAW samples](image)

A Miller Dynasty 300 LX constant current GTAW power supply was remote triggered by the arc voltage control on the Jetline machine was used to provide arc-welding current. The shielding gases used were pure Argon, Argon mixed with 2% N₂, and Argon mixed with 5% N₂. Sample A (A in Figure 4.6) was welded with 20 cfh Ar shielding gas and 4.9in/min travel speed with a welding current of 150A. Sample B was welded with 20 cfh Ar + 2% N₂ shielding gas and 4in/min travel speed with a
welding current of 150A. Sample C was welded using the same conditions as Sample B, except for a travel speed of 6in/min. Sample A was sectioned after welding for further DHCT from the upper left strip. Sample B and C were sectioned out from the lower right strip. Sample D was welded manually by autogenous GTAW with 20 cfh Ar shielding gas and a welding current of 150A together with a 26Cr-1Mo shim as filler metal. Sample E was welded with 20 cfh Ar + 5% N₂ shielding gas and 4in/min travel speed with a welding current of 150A. At least 2-3 samples of ~0.3 in. width were prepared for each welding condition. Detailed welding parameters and conditions are shown in Table 4.4. The geometry sketch of sample after sectioning is shown in Figure 4.7, and actual sample is shown in Figure 4.8.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Shielding Gas</th>
<th>Welding Method</th>
<th>Current</th>
<th>Travel Speed</th>
<th>Heat Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>Pure Argon</td>
<td>Autogenous GTAW</td>
<td>150A</td>
<td>4.9 in/min</td>
<td>27 kJ/in</td>
</tr>
<tr>
<td>Sample B</td>
<td>Argon w/ 2% N₂</td>
<td>Autogenous GTAW</td>
<td>150A</td>
<td>4 in/min</td>
<td>33 kJ/in</td>
</tr>
<tr>
<td>Sample C</td>
<td>Pure Argon</td>
<td>Autogenous GTAW</td>
<td>150A</td>
<td>6 in/min</td>
<td>22 kJ/in</td>
</tr>
<tr>
<td>Sample E</td>
<td>Argon w/ 5% N₂</td>
<td>Autogenous GTAW</td>
<td>150A</td>
<td>4 in/min</td>
<td>33 kJ/in</td>
</tr>
</tbody>
</table>
Figure 4.7: DHCT sample sketch after autogenous GTAW on top and bottom surfaces

Figure 4.8: DHCT sample after autogenous GTAW on top and bottom surfaces
4.3 Design of Gleeble HAZ Simulated Samples

Gleeble ® 3800 system is the mechanical physical simulator using resistive heating. It can reproduce many metallurgical phenomena occurring during the welding process. A type K control thermocouple was welded at the center of the test sample using a thermocouple spot welder to record the temperature. The thermal control system is formed by welding the thermocouples to surface of the center of test specimens providing precise temperature control. Dilatometer was set at the center of the sample to measure the diametric dilation change of the sample during thermal simulation. For the HAZ simulated samples, they are 10mm in diameter by 100mm long rods. Eighteen samples were prepared for simulation in total, and three samples were simulated for each heating and cooling condition. The set up of sample in Gleeble system is shown in Figure 4.9.
During the simulation, samples were heated up to 1340°C by the rate of 100°C/s. The cooling rate was defined by $t_{12/8}$, which is the cooling time from 1200°C to 800°C. Without holding at peak temperature, the samples were air-cooled, and the cooling rate was controlled by six different free span distances between copper jaw grips. The range of the final cooling rates is from 8°C/s to 112°C/s. The detailed thermal histories of HAZ simulated samples are shown in Figure 4.10. The results in terms of cooling rate and ferrite content are shown in Table 4.5 below. The cooling rates and sample design described above is the first round of Gleeble HAZ simulated sample. The second round of Gleeble HAZ simulated samples is following the same
cooling rate choices, but with the sample design similar with autogenous welded samples.

Figure 4.10: Thermal histories of HAZ simulated samples, DSS 2205
Table 4.5: Gleeble simulated samples and base metal sample cooling rate and ferrite percentage

<table>
<thead>
<tr>
<th></th>
<th>Cooling Rate</th>
<th>Free Span</th>
<th>Ferrite Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Metal Sample</td>
<td></td>
<td></td>
<td>49%</td>
</tr>
<tr>
<td>Simulated Sample</td>
<td>8°C/s</td>
<td>70mm</td>
<td>39%</td>
</tr>
<tr>
<td></td>
<td>14 °C/s</td>
<td>50mm</td>
<td>40.5%</td>
</tr>
<tr>
<td></td>
<td>21 °C/s</td>
<td>35mm</td>
<td>43.5%</td>
</tr>
<tr>
<td></td>
<td>33 °C/s</td>
<td>25mm</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>47 °C/s</td>
<td>20mm</td>
<td>53%</td>
</tr>
<tr>
<td></td>
<td>112 °C/s</td>
<td>10mm</td>
<td>71%</td>
</tr>
</tbody>
</table>

One primary advantage of using Gleeble is that a relatively large volume of a distinct microstructure can be produced in a single test specimen with precise temperature control. This allows for precisely replicating the microstructural regions in bulk test specimens, such as the regions in HAZ that are difficult to analyze or extract from an actual weldment.
4.4 Delayed Hydrogen Cracking Test (DHCT)

The DHCT has been developed as a tool for evaluation and ranking susceptibility to hydrogen assisted cracking in welded joints subjected to service in hydrogen containing environments. A test sample is loaded with a constant tensile load, typically 90% of the tested yield strength of material, during continuous electrolytic charging with hydrogen. The frame is designed to allow simultaneous hydrogen charging and loading, which incorporates a 10:1 lever arm ratio shown in Figure 4.11.

Figure 4.11: DHCT frame with the 10:1 lever arm$^{20}$
The triangle pivots and pivot blocks are used to align the sample linearly so that there is not bending of the sample experienced during testing. A clevis system is also incorporated in the DHCT frame design to provide a place for securing the samples in the frame set-up and to further reduce bending on the sample. Both the triangle pivots and pivot blocks have a load bearing capacity of 641MPa. Sample elongation is measured by a linear variable differential transformer (LVDT). The LVDT records the time to failure (TTF) for each sample at the end of the loading arm. The TTF is used as a ranking criterion for susceptibility to hydrogen assisted cracking and for evaluation of the effects of materials composition, microstructure, and fabrication procedures. The overall DHCT setup is shown in Figure 4.12.

![DHCT setup image](image)

**Figure 4.12: DHCT set-up**

- a) Test Frame;
- b) Electrolytic Cell
The test sample gauge section contains the region of interest that can be an actual weld (weld metal and HAZ) or simulated HAZ. The sample (cathode) is immersed in an electrolytic cell where the gauge section is exposed to a solution of 0.1N sulfuric acid (H₂SO₄) and 0.1 g/l sodium thiosulfate (Na₂S₂O₃) in distilled water, and is charged with hydrogen under constant current density of 10 mA/cm². The pH of the electrolyte is maintained within the range of 1.10-1.12. All charging procedures are performed at room temperature with continuous recirculation of the electrolyte via the peristaltic pumps and stirring devices (in the 5-gallon electrolytic containers) to maintain a constant pH through the testing.

The samples (shown in Figure 4.8) are prepared by drilling two holes in the grip section in order to fit in the mounting fixture of the DHCT test frame. After welding and Gleeble simulation, the sample surface need to be cleaned with 600-grit polish paper and ethyl alcohol. Next, using nail polish and two layers of plasti-dip to coat the sample in order to only expose the weld metal and HAZ areas in the electrolyte.

After installing in the electrolytic cell, the test sample is loaded to 90% of its yield strength, the charging current is turned on, and the cell filled with electrolyte. During the test, the LVDT signal is continuously monitored using a data acquisition system to determine sample elongation and time to failure. The initial DHCT load (90% of yield strength) is determined by a tensile test of a DHCT test sample for each of the different welding and heat treatment conditions.
For the weld configuration used in this study (Figure 4.6), the DHCT samples were loaded in tension normal to the rolling direction of the plate. This represents the worst-case scenario of weld orientation in terms of combined tensile loading and simultaneous charging with hydrogen during service.

When the sample failed during the DHCT, the proper cleanup procedure should be performed to remove the residual acid to avoid corrosion and further damage to the fracture surface. First, the data from LVDT should be saved properly. Next, the sample is cleaned by water and ethyl alcohol followed by ultrasonicator to remove contaminated, nail polish, and moisture on the fracture surface.

4.5 Mechanical Testing

In order to determine the accurate yield strength used for the samples, tensile testing was utilized. The MTS 810 Material Test System with a 500kN load capacity was used to test the tensile samples. Strain rate maintained throughout the test was 0.5mm/s. The results of yield strength from tensile test were used for DHCT of welded samples.

4.6 Characterization

Samples for metallurgical analysis were mounted and polished through 1µm diamond and then etched with etchant 220 (electrolytic sodium hydroxide etch).35
Light optical microscopy was used to take images for further metallurgical analysis. As required by ASTM E562-11, systematic manual point counting for determining volume fraction was used to measure the ferrite content. Ferrite contents measured by volume fraction analysis over photoshopped images and Feritscope will be further listed together as comparison. Optical images were taken at locations as listed in Figure 4.13 at 500X magnification using image processing program ImageJ to place 10 lines horizontally and 10 lines vertically to create 100 intersection points. The total points that fall within ferrite phase were counted to determine the volume fraction ferrite. Fractography was performed on the failed DHCT samples. A Quanta 200 and XL-30 ESEM were used to capture images of the fracture surfaces.
Figure 4.13: WM and HAZ optical images locations
Chapter 5 Results & Discussions

5.1 Metallurgical Characterization of Welded Samples

In order to have better understanding of the failure mechanism and susceptible microstructure to HAC, metallurgical characterization is very important for this study. The main focus is on the ferrite content in WM and HAZ after welding. The analysis of microstructure and ferrite content at weld metal and HAZ for each welding condition used the tools of optical microscopy, scanning electron microscopy, and ASTM E562-11 systematic manual point counting for determining volume fraction.

The microstructures of heat affected zone and weld metal after welding are shown in Figures 5.1. The images are from sample A in second pass. From point counting method, HAZ had 56% ferrite content and WM had 85% ferrite content. Base metal still stays around 50% ferrite content.
The microstructure in second pass welds of samples A, B, C, and D is shown in Figures 5.2 and sample E in Figure 5.3. The weld metal ferrite content in the first and second pass welds, determined using the ASTM E562-11 point counting procedure, is summarized in Table 5.1. The applied welding procedures generated the desired wide range of weld metal ferrite contents (between 56% and 91%). For the check of the accuracy of point counting method, image analysis of optical images was conducted with the help of image processing softwares ImageJ and Photoshop. The results are shown in Figures 5.4, which are relatively close to the results from the point counting method that industry suggested.

Reheating of the weld metal in multipass welds in DSS can result in a reduction of the original weld metal ferrite content, since the ferrite is metastable due to rapid cooling from elevated temperature. As shown in Table 5.1, the first pass weld metal
in all tested welds had lower ferrite content than the second pass, typically by 10-20 vol%. This is attributed to the growth of the existing austenite and also to the formation of secondary austenite within the ferrite grains.

A comparison of the weld metal ferrite content in samples B and C confirms the anticipated effect of lowering the heat input on increasing ferrite content. Comparison of samples A and C shows that adding nitrogen to the shielding gas has effect in reducing the ferrite content by promoting the austenite. Sample D had the highest weld metal ferrite content of all test welds, which is related to increasing the Cr$_{eq}$ of the weld metal by dilution from the 26Cr–1Mo shim.

The HAZ ferrite content is not completely consistent with the observations in the weld metal, because it is only affected by heat input and cooling rate. This can also be attributed to the inherent difficulties in evaluation of HAZ ferrite content related to the narrow width and strong microstructural gradients present in these low heat input welds.
Figure 5.2: Ferrite content of Sample A, B, C, and D in 2\textsuperscript{nd} pass weld metal (500X)
Figure 5.3: Ferrite content of Sample E in 2\textsuperscript{nd} pass (Left HAZ: 62\%, Right WM: 54\%)
(a) Sample A with 74% ferrite  
(b) Sample B with 58% ferrite  
(c) Sample C with 59% ferrite  
(d) Sample D with 89% ferrite  

Figure 5.4: Ferrite content image analysis of Sample A, B, C, and D in 2\textsuperscript{nd} pass weld metal
Table 5.1: Weld Metal and HAZ Ferrite Content (ASTM 562-11)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shielding Gas</th>
<th>Travel Speed</th>
<th>Heat Input</th>
<th>1st Pass</th>
<th>2nd Pass</th>
<th>1st Pass WM</th>
<th>2nd Pass WM</th>
<th>Image Analysis</th>
<th>Feritscope</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20cfh Ar</td>
<td>4.9in/min</td>
<td>27 kJ/in HI</td>
<td>75%</td>
<td>56%</td>
<td>64% (reheated)</td>
<td>85%</td>
<td>74%</td>
<td>59%</td>
</tr>
<tr>
<td>B</td>
<td>20cfh Ar+ 2% N₂</td>
<td>4in/min</td>
<td>33 kJ/in</td>
<td>65%</td>
<td>71%</td>
<td>60% (reheated)</td>
<td>67%</td>
<td>58%</td>
<td>57%</td>
</tr>
<tr>
<td>C</td>
<td>20cfh Ar+ 2% N₂</td>
<td>6in/min</td>
<td>22 kJ/in</td>
<td>68%</td>
<td>58%</td>
<td>61% (reheated)</td>
<td>72%</td>
<td>59%</td>
<td>58%</td>
</tr>
<tr>
<td>D</td>
<td>20cfh Ar with 26Cr-1Mo shim</td>
<td>Manual Autogenous GTAW</td>
<td>Heat Input ~20 kJ/in</td>
<td>71%</td>
<td>68%</td>
<td>81% (reheated)</td>
<td>91%</td>
<td>89%</td>
<td>67%</td>
</tr>
<tr>
<td>E</td>
<td>20cfh Ar with 26Cr-1Mo shim</td>
<td>4in/min</td>
<td>33 kJ/in</td>
<td>54%</td>
<td>62%</td>
<td>53% (reheated)</td>
<td>54%</td>
<td>N/A</td>
<td>55%</td>
</tr>
</tbody>
</table>
5.2 Metallurgical Characterization of Gleeble Simulated Samples

Using Gleeble® to control the thermal history gives different microstructures under $t_{12/8}$ cooling rates based on the cooling time from 1200°C to 800°C. In this case, heat affected zones undergoing different cooling rates were simulated by showing significantly varied ferrite contents. The result of different cooling rates based on different free span distances together with its ferrite content is shown in Table 5.2.

<table>
<thead>
<tr>
<th></th>
<th>Cooling Rate</th>
<th>Free Span</th>
<th>Ferrite Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Metal Sample</td>
<td>8°C/s</td>
<td>70mm</td>
<td>39%</td>
</tr>
<tr>
<td>Simulated Samples</td>
<td>14°C/s</td>
<td>50mm</td>
<td>41%</td>
</tr>
<tr>
<td></td>
<td>21°C/s</td>
<td>35mm</td>
<td>44%</td>
</tr>
<tr>
<td></td>
<td>33°C/s</td>
<td>25mm</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>47°C/s</td>
<td>20mm</td>
<td>53%</td>
</tr>
<tr>
<td></td>
<td>64°C/s</td>
<td>15mm</td>
<td>55%</td>
</tr>
<tr>
<td></td>
<td>112°C/s</td>
<td>10mm</td>
<td>71%</td>
</tr>
</tbody>
</table>
Given the ferrite content above, 39% ferrite content sample with 8°C/s cooling rate, 53% ferrite content sample with 47°C/s cooling rate, and 71% ferrite content sample with 112°C/s cooling rate were picked for delayed hydrogen cracking test. The microstructures are shown in Figures 5.5 below.

(a) Base metal with 49% ferrite
(b) 39% ferrite content sample
(c) 53% ferrite content sample
(d) 71% ferrite content sample

Figure 5.5: Ferrite content of base metal and chosen HAZ simulated samples (500X)
After using the wrong yield strength data from MTR report for DHCT on first round of Gleeble HAZ simulated samples, the samples didn't fail as predicated. The second round of samples was simulated under the same cooling rate conditions in order to reproduce the samples for DHCT. With limited time for this study, DHCT on second
round of Gleeble HAZ simulated samples are not finished and will be included in the future work.

5.3 Susceptibility to Hydrogen Assisted Cracking

The DHCT displacement-time plots are shown in Figure 5.6 for the samples described in Table 5.1. There is a direct correlation between the ferrite content of the second pass, and elongation at failure and TTF. Sample D with 91% ferrite failed in 8 hours with almost no elongation, followed by sample A with 85% ferrite/74 hours at an elongation of 81 microns, sample C with 71% ferrite/106 hours at an elongation of 204 microns, sample B with 67% ferrite/203 hours at elongation of around 236 microns, and sample E with 54% ferrite/450 hours at elongation of more than 250 microns. A summary of ferrite content and DHCT failure results are listed in Table 5.3.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Ferrite Content</th>
<th>Time to Failure, hrs</th>
<th>Failure Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>1st pass: 75% in HAZ, 64% in WM 2nd pass: 56% in HAZ, 85% in WM</td>
<td>A1 73.9  A2 76</td>
<td></td>
</tr>
<tr>
<td>Sample B</td>
<td>1st pass: 65% in HAZ, 60% in WM 2nd pass: 71% in HAZ, 67% in WM</td>
<td>B1 202.5  B2 190</td>
<td></td>
</tr>
<tr>
<td>Sample C</td>
<td>1st pass: 68% in HAZ, 61% in WM 2nd pass: 58% in HAZ, 72% in WM</td>
<td>C1 106.3</td>
<td>Weld Metal</td>
</tr>
<tr>
<td>Sample D</td>
<td>1st pass: 71% in HAZ, 81% in WM 2nd pass: 68% in HAZ, 91% in WM</td>
<td>D1 8.1</td>
<td></td>
</tr>
<tr>
<td>Sample E</td>
<td>1st pass: 54% in HAZ, 53% in WM 2nd pass: 62% in HAZ, 54% in WM</td>
<td>E1: 19  E2: 450</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.7: DHCT results of Sample A, B, C, D, & E
5.4 Failure Mechanism

All test samples failed initially in the second pass weld metal with higher ferrite content, then ultimately failed by overloading through the first pass. An example of this failure mechanism is illustrated in Figure 5.7 which shows a cross section through the gage section and the appearance of the 1st and 2nd weld surface. Note that multiple hydrogen assisted cracks nucleated on the surface of the 1st pass weld in sample B after the higher ferrite content 2nd pass surface already cracked. The ultimate failure occurred in the weld metal by propagation of the crack nucleated in the second pass weld.

The fracture morphology from samples A and B is shown in Figures 5.8 and 5.9. The higher ferrite content 2nd pass sides in both DHCT samples exhibit brittle fracture consisted of quasi cleavage morphology. The latter represent typical crack nucleation and propagation mechanisms of hydrogen assisted cracking at high hydrogen concentration and lower stress intensity. The final crack propagation and failure occurred through the first pass weld by overloading through a ductile microvoid coalescence mechanism.
Figure 5.8: Hydrogen assisted cracking failure in sample B
Figure 5.9: Fracture surfaces of sample A & B showing brittle quasi cleavage and intergranular morphology in the second pass weld and ductile micro-void coalescence morphology in the first pass weld.

Figure 5.10: Examples of intergranular, quasi cleavage (left), and microvoid coalescence (right) from the regions indicated in Sample A (Figure 5.8).
The results show a very strong effect of the weld phase balance on the susceptibility to hydrogen assisted cracking in autogenous GTA welds of 2205 duplex stainless steel. Increasing the weld metal ferrite content from 54% to 91% resulted in a significant reduction of the time-to-failure in the Delayed Hydrogen Cracking Test (DHCT) from 450 hours to 8 hours.

The crack nucleation and propagation in the DHCT samples occurred in the higher ferrite pass of overlapping two pass welds where reheating of the initial pass by the second pass resulted in a reduction in the ferrite content. This occurs due to the metastable nature of the weld metal ferrite in welds with high ferrite content made at low heat input. Crack nucleation and growth in the high ferrite weld metal occurred by a mixture of quasi-cleavage and intergranular fracture modes. Final sample failure occurred by overload through the lower ferrite content weld metal and exhibited a microvoid coalescence fracture mode. This failure mechanism closely reproduced the actual service failures in REAC welds.

The DHCT exhibited high sensitivity and good reproducibility in determining the effect of weld metal ferrite content on hydrogen assisted cracking susceptibility in autogenous GTA welds of DSS 2205. This appears to be an effective method to evaluate the effect of ferrite/austenite balance on HAC in both the weld metal and HAZ.
Additional testing is needed to further examine the reproducibility of the DHCT and to establish guidelines for the maximum ferrite content in 2205 welds that will prevent service failures. These guidelines are expected to conform to the industrial experience of no REAC failures in 2205 welds with approximately 60% ferrite. The initial results of this study are consistent with that industrial experience.
Chapter 6 Conclusion

6.1 Gas Tungsten Arc Weld Metal

- Lower heat input and Nitrogen balanced shielding gas are recommended to stabilize the weld metal ferrite content.
- Reheating effects in multi-pass welds tend to reduce the ferrite content of the weld by promoting transformation of metastable ferrite.
- Results from the Delayed Hydrogen Cracking Test (DHCT) show a strong influence of ferrite/austenite balance on HAC resistance.

90 vol% ferrite → 8 hours to failure

80 vol% ferrite → 75 hours to failure

70 vol% ferrite → 100 hours to failure

60 vol% ferrite → 200 hours to failure

50 vol% ferrite → 450 hours to failure
6.2 Gleeble® HAZ Simulated Samples

- HAZ ferrite content is dependent on cooling rate. Slower cooling rate can lower the HAZ ferrite content.
- Tensile testing of actual DHCT samples is necessary to acquire accurate yield strength data needed for determination of the load in DHCT testing.
- Point counting is still the most accurate method for quantification of the ferrite content in small-scaled microstructures.

6.2 Weld Metal Failure Mechanism

- Crack nucleation and growth occurred in the non-reheated higher ferrite second pass of the weld metal by brittle quasi-cleavage and intergranular mechanisms. The complete sample failure occurred through the reheated lower ferrite first pass of the weld by ductile microvoid coalescence. The failure mechanism closely reproduced the actual service failures in REAC welds.
- The DHCT is an effective method for evaluation of the effect of ferrite/austenite balance on HAC susceptibility in both the weld metal and HAZ of duplex stainless steel welds.
Chapter 7 Future Work

1. Second round of Gleeble HAZ simulation – DHCT
2. Compare DHCT results from autogenous GTAW samples with Gleeble HAZ simulated samples with correct yield strength from tensile testing
3. Metallography and DHCT on mock-up samples prepared by Shell to validate resistance to HAC, and compare DHCT results with autogenous GTAW samples and Gleeble samples
4. Suggestions & recommendations on future fabrication method and preferred welding parameters and procedures for DSS 2205 REAC systems
References


Appendix A: Sample Design Sketches

Figure A.1: DHCT Sample Design for Gleeble Samples
Figure A.2: DHCT Sample Design for GTAW and Mock Up Samples
Figure A.3: DHCT Sample Machine Plan from Mock Up Sample
Appendix B: Fractography for Sample C, and D

Figure B.1: Sample C
Figure B.2: Sample D
Appendix C: PVP Conference Proceeding Paper (2016)
EVALUATION OF THE SUSCEPTIBILITY OF DUPLEX STAINLESS STEEL
2205 TO HYDROGEN ASSISTED CRACKING IN REAC SYSTEMS

Mei He
The Ohio State University
Columbus, Ohio, USA
He.321@buckeyemail.osu.edu

John Lippold & Boian Alexandrov
The Ohio State University
Columbus, Ohio, USA
Lippold.1@osu.edu & Alexandrov.1@osu.edu

Jorge Penso
Shell Global Solutions (US), Inc.
Houston, Texas, USA
Jorge.penso@shell.com

ABSTRACT

Duplex stainless steel (DSS) is one material choice to fabricate the reactor effluent air cooler (REAC) of hydrocracker units in order to improve the performance and service lifetime of these units. Unfortunately, several failures from around the world have been reported in REAC units constructed of DSS, some within five years of service. Based on failure analysis reports, the failures were generally associated with welded joints and were caused by crevice/pitting corrosion and stress corrosion cracking. Given the condition of hydrogen-rich environment, high-pressure process fluid, and service temperature, this type of cracking is most likely a form of hydrogen assisted cracking (HAC). It is highly influenced by phase balance (ferrite/austenite) after welding and welding procedures, with high levels of ferrite in the weld metal or HAZ increasing the susceptibility to HAC. In this study, different weld metal phase balances were prepared by autogenous gas tungsten arc welding (GTAW). The delayed hydrogen cracking test (DHCT) was used to evaluate the effects of the weld phase balance on the susceptibility to HAC in DSS 2205 welds. Using this approach, weld metal ferrite levels on the order of 90 vol% ferrite led to very rapid failure, while reducing the ferrite level to approximately 60 vol% greatly increased resistance to HAC.

1. INTRODUCTION

Around 8-10 cases of DSS REAC failures have been reported around the world, in some cases leading to fire and explosion. The REAC is part of the hydrocracker unit, which is
used to produce maximum distillates of high-speed diesel, kerosene, naphtha and liquefied petroleum gas (LPG). During the sulfur removal procedure, the reactions occur at high temperature in presence of hydrogen. The process stream containing hydrogen sulfide (H2S), ammonia (NH3) and hydrogen chloride (HCl) after reactions enters REAC, which separates the hydrogen-rich vapor, hydrocarbon liquid, and water.

In most of the failure scenarios, cracking was located between either the top plate and tube sheet, or bottom plate and tube sheet of the header box. Metallurgical investigation of the failures revealed high ferrite content at the location of cracking, suggesting that the high ferrite levels in the weld metal and HAZ contribute to HAC. Fractographic analysis of these failures showed a mixture of ductile and brittle fracture modes.

Based on the assumption that HAC is the predominant failure mode and the observed presence of high ferrite levels at the failure locations, this study was designed to evaluate the relationship between ferrite content and HAC susceptibility in DSS 2205 welds. Samples with different phase balance (ferrite/austenite) were prepared using the GTAW process with different welding parameters and shielding gases. The delayed hydrogen cracking test (DHCT) was then used to evaluate the susceptibility to HAC. The sample during DHCT is loaded with a constant tensile stress (90% yield strength) and simultaneously charged with hydrogen in a continuous circulation of pH 1.10-1.12 electrolyte. Metallurgical characterization and ferrite content measurement techniques were used to quantify the phase balance as a function of different welding conditions. Fractographic analysis was performed on failed DHCT samples to determine the fracture morphologies and failure mechanism.

2. BACKGROUND

Duplex stainless steels are known for their superior corrosion resistance and strength relative to plain carbon steel, which are the primary reasons to be a choice for REAC fabrication. With high levels of chromium and low to moderate amounts of nickel and a balanced microstructure of approximately equal volume percentages of ferrite and austenite, these materials have exhibited resistance to both stress corrosion cracking and pitting in a variety of environments. Based on corrosion resistance, these steels are designated as “lean” (2101, 2003), “conventional” (2205), “super” (2507), and “hyper” (2707, 3207). The conventional DSS 2205 is one choice for use in the REAC systems and is the alloy used in this study.

Phase balance (ferrite/austenite) is a critical factor related to toughness, corrosion resistance, and potentially HAC susceptibility, with high ferrite levels leading to a
degradation of each of these properties. Base metal processing produces a 50/50 phase balance and results in optimum properties. High ferrite content in the weld metal and HAZ of these steels can increase susceptibility to HAC if sufficient hydrogen and stress are present. Controlling the balance of ferrite and austenite in the DSS welds is the best insurance against HAC.  

During solidification, DSS 2205 solidifies to a completely ferritic structure then transforms to austenite upon cooling below the ferrite solvus. This transformation is controlled by a combination of composition and cooling rate. For a given composition, as the cooling rate increases the weld metal and HAZ ferrite content increases. As a result, welding conditions (heat input) can have a major influence on the weld phase balance. The addition of nitrogen to the shielding gas can also influence phase balance, since nitrogen is a strong austenite stabilizer. In this study, both heat input and shielding gas were used to produce a range of weld metal ferrite levels.

For HAC in DSS 2205 welds, there is no detailed explanation of the mechanism. The factors that can influence the susceptibility to HAC are microstructure (ferrite/austenite phase balance), hydrogen concentration, loading conditions, and temperature. In this study, the focus is on the effect of ferrite/austenite phase balance on HAC susceptibility using DHCT, since phase balance can be controlled in actual practice by a combination of material selection and welding conditions. The experimental method used in this study evaluates HAC susceptibility based on the microstructure in DSS 2205 welds as determined by a comparison of time to failure of samples charged with hydrogen and loaded to a constant fraction of the yield stress.

3. OBJECTIVES

Based on recent failures in REAC systems built using DSS 2205, it is necessary to better understand the failure mechanism and to determine the relationship between HAC susceptibility and the ferrite/austenite phase balance. Moreover, once the effect of microstructure is determined, other factors of HAC susceptibility such as welding process and weld joint geometry can be evaluated.

1) Determine the effect of the weld phase balance and microstructure on the susceptibility to HAC in DSS 2205 welds (weld metal and HAZ) using the DHCT.

2) Provide recommendations on selection of base and filler metal compositions, welding processes/parameters, and weld joint geometry that will reduce the risk of HAC in REAC systems.
4. MATERIALS & PROCEDURES

4.1 MATERIALS

DSS 2205 plate was used in this study for the production of all the autogenous GTAW samples. The composition of the base metal is listed in Table 1 and the microstructure is shown in Figure 1.

Using the WRC-1992 diagram, the Cr(eq) is 25.86 and Ni(eq) is 9.5. The weld metal ferrite number estimate based on this composition is FN 98 which equates to a level of approximately 70 vol% ferrite. In order to increase the ferrite content of the weld metal above this level, a ferritic stainless steel (26Cr-1Mo) shim (Table 1) was used with autogenous GTAW to create a level of 90% ferrite content, as describe in the following section.

Table 1: Chemical composition (wt%) of DSS 2205 steel and 26Cr-1Mo shim (nominal)

<table>
<thead>
<tr>
<th>Material</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cu</th>
<th>Co</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSS 2205</td>
<td>22.5</td>
<td>5.74</td>
<td>3.35</td>
<td>1.32</td>
<td>0.19</td>
<td>0.11</td>
<td>0.32</td>
<td>0.009</td>
<td>0.17</td>
<td>0.006</td>
</tr>
<tr>
<td>26Cr-1Mo Shim</td>
<td>26.0</td>
<td>0.15</td>
<td>1.0</td>
<td>0.05</td>
<td>0.02</td>
<td>0.002</td>
<td>0.20</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>
4.2 DESIGN OF WELDED SAMPLES

For further use for DHCT, plate of 12in length by 12in width with 0.5in thickness was machined to four 3 in. wide strips with a 1 in. x 0.2 in. gauge section, as shown in Figure 2. In this configuration, the welds were oriented parallel to the plate rolling direction.

Sample A (A in Fig. 2) was welded with 20 cfh Ar shielding gas and 4.9in/min travel speed with a welding current of 150A. Sample B was welded with 20 cfh Ar + 2% N2 shielding gas and 4in/min travel speed with a welding current of 150A. Sample C was welded using the same conditions as Sample B, except for a travel speed of 6in/min. Sample A was sectioned after welding for further DHCT from the upper left strip. Sample B and C were sectioned out from the lower right strip. Sample D was welded manually by autogenous GTAW with 20 cfh Ar shielding gas and a welding current of 150A together with a 26Cr-1Mo shim as filler metal. At least 2-3 samples of ~ 0.3 in. width were prepared for each welding condition. Detailed welding parameters and conditions are shown in Table 2. The sample geometry after sectioning is shown in Figure 3.
Table 2: Welding Parameters for Samples A, B, C, and D

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Shielding Gas</th>
<th>Welding Method</th>
<th>Current</th>
<th>Travel Speed</th>
<th>Heat Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>Pure Argon</td>
<td>Autogenous GTAW</td>
<td>150A</td>
<td>4.9 in/min</td>
<td>27 kJ/in</td>
</tr>
<tr>
<td>Sample B</td>
<td>Argon w/ 2% N₂</td>
<td>Autogenous GTAW</td>
<td>150A</td>
<td>4 in/min</td>
<td>33 kJ/in</td>
</tr>
<tr>
<td>Sample C</td>
<td>Pure Argon [26Cr-1Mo</td>
<td>Autogenous GTAW</td>
<td>150A</td>
<td>6 in/min</td>
<td>22 kJ/in</td>
</tr>
<tr>
<td>Sample D</td>
<td>Pure Argon [26Cr-1Mo</td>
<td>Manual GTAW</td>
<td>150A</td>
<td>Manual</td>
<td>~20kJ/in</td>
</tr>
</tbody>
</table>
4.3 DELAYED HYDROGEN CRACKING TEST

The DHCT has been developed as a tool for evaluation and ranking susceptibility to hydrogen assisted cracking in welded joints subjected to service in hydrogen containing environments. A test sample is loaded with a constant tensile load, typically 90% of the tested material yields strength, during continuous electrolytic charging with hydrogen. The test sample gauge section contains the region of interest that can be an actual weld (weld metal and HAZ) or simulated HAZ. The sample (cathode) is immersed in an electrolytic cell where the gauge section is exposed to a solution of 0.1n H₂SO₄ and 0.1 g/l Na₂S₂O₃ in distilled water, and is charged with hydrogen under constant current density of 10 mA/cm². The pH of the electrolyte is maintained within the range of 1.10-1.12. A linear variable differential transducer (LVDT) is used to record the time-to-failure (TTF) and to measure sample elongation during the DHCT procedure. The TTF is used as a ranking criterion for susceptibility to hydrogen assisted cracking and for evaluation of the effects of materials composition, microstructure, and fabrication procedures.
The overall DHCT setup is shown in Figure 4. The samples (shown in Fig. 3) are prepared by drilling two holes in the grip section in order to fit in the mounting fixture of the DHCT test frame. The sample outside the gage section is coated with nail polish and two layers of plasti-dip from Performix in order to expose only the weld metal and HAZ areas in the electrolyte.

After installing in the electrolytic cell, the test sample is loaded to 90% of its yield strength, the charging current is turned on, and the cell filled with electrolyte. During the test, the LVDT signal is continuously monitored using a data acquisition system to determine sample elongation and TTF. The initial DHCT load (90% of yield strength) is determined by a tensile test of a DHCT test sample for each of the different welding conditions.

For the weld configuration used in this study (Figure 2), the DHCT samples were loaded in tension normal to the rolling direction of the plate. This represents the worst case scenario of weld orientation in terms of combined tensile loading and simultaneous charging with hydrogen during service.
4.4 CHARACTERIZATION

Samples for metallurgical analysis were mounted and polished through 1μm diamond and then etched with etchant 220 (electrolytic sodium hydroxide etch). Light optical microscopy was used to take images for further metallurgical analysis. As required by ASTM E562-11, systematic manual point counting for determining volume fraction was used to measure the ferrite content. Optical images were taken at locations as listed in Figure 5 at 500X magnification using image processing program ImageJ to place 10 lines horizontally and 10 lines vertically to create 100 intersection points. The total points that fall within ferrite phase were counted to determine the volume fraction ferrite.

Fractography was performed on the failed DHCT samples. A Quanta 200 and XL-30 ESEM were used to capture images of the fracture surfaces.

5. RESULTS & DISCUSSIONS

5.1 METALLURGICAL CHARACTERIZATION

The microstructure in second pass welds of samples A, B, C, and D is shown in Figures 6. The weld metal ferrite content in the first and second pass welds, determined using the ASTM E562-11 point counting procedure, are summarized in Table 3. The applied welding procedures generated the desired wide range of weld metal and HAZ ferrite contents (between 56% and 91%). The results also showed that WRC 1992 diagram FN from section 4.1 can not accurately predict the ferrite content in DSS 2205 welds made
over a range of heat input and cooling rate conditions. They will change austenite/ferrite microstructure balance very efficiently even with additional Nickel and Nitrogen content as austenite stabilizers from base metal.

Reheating of the weld metal in multipass welds in DSS can result in a reduction of the original weld metal ferrite content, since the ferrite is metastable due to rapid cooling from elevated temperature. As shown in Table 3, the first pass weld metal in all tested welds had lower ferrite content than the second pass, typically by 10-20 vol%. This is attributed to the growth of the existing austenite and also to the formation of secondary austenite within the ferrite grains.\textsuperscript{13-14}

A comparison of the weld metal ferrite content in samples B and C confirms the anticipated effect of lowering the heat input on increasing ferrite content. Comparison of samples A and C shows that adding nitrogen to the shielding gas has stronger effect in reducing the ferrite content than increasing the heat input.\textsuperscript{7} Sample D had the highest weld metal ferrite content of all test welds, which is related to increasing the Creq of the weld metal by dilution from the 26Cr–1Mo shim.

The HAZ ferrite content is not completely consistent with the observations in the weld metal. This can be attributed to the inherent difficulties in evaluation of HAZ ferrite content related to the narrow width and strong microstructural gradients present in these low heat input welds.
(a) Sample A with 85% ferrite   (b) Sample B with 67% ferrite

(c) Sample C with 72% ferrite   (d) Sample D with 91% ferrite

Figure 6: Ferrite content of Sample A, B, C, and D in 2\textsuperscript{nd} pass weld metal
Table 3: Weld Metal and HAZ Ferrite Content (ASTM 562-11)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ferrite Content (vol%)</th>
<th>HAZ</th>
<th>Weld Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>75%</td>
<td>64% (reheated)</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>56%</td>
<td>85%</td>
</tr>
<tr>
<td>B</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>65%</td>
<td>60% (reheated)</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>71%</td>
<td>67%</td>
</tr>
<tr>
<td>C</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>68%</td>
<td>61% (reheated)</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>58%</td>
<td>72%</td>
</tr>
<tr>
<td>D</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>71%</td>
<td>81% (reheated)</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>68%</td>
<td>91%</td>
</tr>
</tbody>
</table>

5.2 SUSCEPTIBILITY TO HYDROGEN ASSISTED CRACKING

The DHCT displacement-time plots are shown in Figure 7 for the four samples described in Table 3. There is a direct correlation between the ferrite content of the second pass, and elongation at failure and TTF. Sample D with 91% ferrite failed in 8 hours with almost no elongation, followed by sample A with 85% ferrite/74 hours at an elongation of 81 microns, sample C with 71% ferrite/106 hours at an elongation of 204 microns, and sample B with 67% ferrite/203 hours at elongation of around 236 microns. A summary of ferrite content and DHCT failure results are listed in Table 4.
Table 4: Weld Metal and HAZ Ferrite Content (ASTM 562-11) & Detailed DHCT Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ferrite Content</th>
<th>Time to Failure, hrs</th>
<th>Failure Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1st pass: 75% in HAZ, 64% in WM 2nd pass: 56% in HAZ, 85% in WM</td>
<td>A1 73.9 A2 76</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1st pass: 65% in HAZ, 60% in WM 2nd pass: 71% in HAZ, 67% in WM</td>
<td>B1 202.5 B2 190</td>
<td>Weld Metal</td>
</tr>
<tr>
<td>C</td>
<td>1st pass: 68% in HAZ, 61% in WM 2nd pass: 58% in HAZ, 72% in WM</td>
<td>C1 106.3</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1st pass: 71% in HAZ, 81% in WM 2nd pass: 68% in HAZ, 91% in WM</td>
<td>D1 8.1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7: DHCT results of Sample A, B, C, & D
5.2 FAILURE MECHANISM

All test samples failed initially in the second pass weld metal with higher ferrite content, then ultimately failed by overloading through the first pass. An example of this failure mechanism is illustrated in Figure 8, which shows a cross section through the gage section and the appearance of the 1\textsuperscript{st} and 2\textsuperscript{nd} weld surface. Note that multiple hydrogen assisted cracks nucleated on the surface of the 1\textsuperscript{st} pass weld in sample B after the higher ferrite content 2\textsuperscript{nd} pass surface already cracked. The ultimate failure occurred in the weld metal by propagation of the crack nucleated in the second pass weld.

The fracture morphology from samples A and B is shown in Figures 9 and 10. The higher ferrite content 2\textsuperscript{nd} pass sides in both DHCT samples exhibit brittle fracture consisted of quasi cleavage and intergranular morphologies. The latter represent typical crack nucleation and propagation mechanisms of hydrogen assisted cracking at high hydrogen concentration and lower stress intensity.\textsuperscript{9} The final crack propagation and failure occurred through the first pass weld by overloading through a ductile microvoid coalescence mechanism.

![Sample B: 2\textsuperscript{nd} Pass Surface (67% Ferrite)](image1)

![1\textsuperscript{st} Pass Surface (60% Ferrite)](image2)

Figure 8: Hydrogen assisted cracking failure in sample B
Figure 9: Fracture surfaces of sample A & B showing brittle quasi cleavage and intergranular morphology in the second pass weld and ductile micro-void coalescence morphology in the first pass weld.

Figure 10: Examples of intergranular, quasi cleavage (left), and microvoid coalescence (right) from the regions indicated in Sample A (Figure 8).
6. SUMMARY

The results of this study show a very strong effect of the weld phase balance on the susceptibility to hydrogen assisted cracking in autogenous GTA welds of 2205 duplex stainless steel. Increasing the weld metal ferrite content from 65% to 91% resulted in a significant reduction of the time-to-failure in the Delayed Hydrogen Cracking Test (DHCT) from 203 hours to 8 hours.

The crack nucleation and propagation in the DHCT samples occurred in the higher ferrite pass of overlapping two pass welds where reheating of the initial pass by the second pass resulted in a reduction in the ferrite content. This occurs due to the metastable nature of the weld metal ferrite in welds with high ferrite content made at low heat input. Crack nucleation and growth in the high ferrite weld metal occurred by a mixture of quasi-cleavage and intergranular fracture modes. Final sample failure occurred by overload through the lower ferrite content weld metal and exhibited a microvoid coalescence fracture mode. This failure mechanism closely reproduced the actual service failures in REAC welds.

The DHCT exhibited high sensitivity and good reproducibility in determining the effect of weld metal ferrite content on hydrogen assisted cracking susceptibility in autogenous GTA welds of DSS 2205. This appears to be an effective method to evaluate the effect of ferrite/austenite balance on HAC in both the weld metal and HAZ.

Additional testing is needed to further examine the reproducibility of the DHCT and to establish guidelines for the maximum ferrite content in 2205 welds that will prevent service failures. These guidelines are expected to conform to the industrial experience of no REAC failures in 2205 welds with approximately 60% ferrite. The initial results of this study are consistent with that industrial experience.

Acknowledgements

This study has been performed within the NSF Manufacturing and Materials Joining Innovation Center (Ma2JIC) and has been supported by Shell Projects and Technology.
References


*Use of Duplex Stainless Steels in the Oil Refining Industry.*


*Welding Duplex and Super-duplex Stainless Steels.*

Duplex Stainless Steels’91. 1, 303-323


