Final Technical Report

**Materials Solutions for Hydrogen Delivery in Pipelines
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Principal Investigator:

Secat, Inc.

FINAL TECHINCAL REPORT

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Recipient:	Secat, Inc., 1505 Bull Lea Road Coldstream Research Campus Lexington, KY 40511
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Contact:	Todd Boggess, (859) 514-4989, tboggess@secat.net
Project Team:	Dr. Monterey Gardiner (DOE-HQ), Dr. Steve Pawel (ORNL) DOE-HQ Project Officer: Paul Bakke DOE- Golden - Award Administrator: Tammie Lawler
Team Members:	G Muralidharan – Oak Ridge National Laboratory John J Koehr - ASME International Dr. Ian Roberson - University of Illinois Dr. Petros Sofronis – University of Illinois Gail Smith – Evraz NA, Oregon Steel Mills Carsten Weinhold - Schott North America – Regional R & D Paul Fisher - Chemical Composite Coatings Int'l, LLC Dr Fahmy Haggag - Advanced Technology Corporation Gary Sullivan - Columbia Gas of Kentucky Doug Stalheim – DGS Metallurgical Solutions Inc. Steve Jansto – Reference Metals Company

Materials Solutions for Hydrogen Delivery in Pipelines

Shridas Ningileri – Secat, Inc.
Doug Stalheim – DGS Metallurgical Solutions, Inc.

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Acknowledgements and Disclaimer

Acknowledgements

Disclaimer

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Abbreviations and Acronyms

ASME -American Society of Mechanical Engineers
ATC - Advanced Technology Corporation
DGS - DGS Metallurgical Solutions, Inc.
DOE – US Department of Energy
DOT – US Department of Transportation
NACE - National Association of Corrosion Engineers
ORNL - Oak Ridge National Laboratory
SEM - Scanning Electron Microscope
SNLL - Sandia National Laboratory – Livermore
TEM - Transmission Electron Microscope
HIC – Hydrogen Induced Cracking
FCGR – Fatigue Crack Growth Rate
YS – Yield Strength
TS – Tensile Strength
RA – Reduction in Area
He – Helium
H_2 – Hydrogen Gas
psi – pounds per square inch
Hz – Hertz
NACE – National Association of Corrosion Engineers
CLR – Crack Length Ratio (ratio of measured crack lengths vs. the coupon length)
CSR – Crack Sensitivity Ratio (ratio of measured cracked cross sectional area vs. coupon cross sectional area)
CTR – Crack Thickness Ratio (ratio of measured crack thickness vs. the coupon thickness)
BHN – Brinell Hardness

Microstructure Abbreviations

AF- Acicular Ferrite
B - Bainite
P - Pearlite
PF - Polygonal Ferrite
UB - Upper Bainite

Executive Summary

Introduction

Gaseous hydrogen is one of several potential fuel sources that can replace fossil fuels in several different sectors of the US economy, especially the transportation (automobiles) and home heating. Supply of these sectors would require large volumes of gaseous hydrogen to be moved economically to major metropolitan. Currently the most economical method for transmission of the volume of hydrogen gas required is under pressure through transmission steel pipelines. As transmission pressures are increased, steel pipelines that could be used for the transport of hydrogen at pressure can be prone to hydrogen embrittlement at the welds, the heat-affected-zone and/or the base metal regions of the pipeline. Over the past few years, significant advances have been made in understanding the mechanisms of hydrogen embrittlement in a wide variety of materials and in materials technologies. However, specific data related to traditional pipeline steels in the presence of gaseous hydrogen under pressure is lacking.

The original objectives of this project were as follows[1]:

1. To identify steel compositions and associated welding filler wires and processes that would be suitable for construction of new pipeline infrastructure
2. To develop barrier coatings for minimizing hydrogen permeation in pipelines and to develop *in-situ* deposition processes suitable for these coatings
3. To understand the cost factors related to the construction of new pipelines and modification of existing pipelines and to identify the path to cost reduction

In support of the three objectives, the following tasks were part of the original program:

1. Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen
2. Develop and/or identify alternate alloys and evaluate hydrogen embrittlement
3. Develop coatings to minimize dissolution and penetration of hydrogen
4. Evaluate the hydrogen embrittlement in alloys coated with selected coatings
5. Perform financial analyses and incorporate knowledge into codes and standards

However, as the project further evolved and with valuable input from the DOE Pipeline Working Group, the key tasks that were agreed upon to focus the work of the project were modified as follows:

1. Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen including the following:
   a. Microstructural characterization – it is known that microstructures play a role in mechanical property performance in the presence of hydrogen.
   b. Mechanical property testing
      i. NACE TM0284 HIC Solution A Testing
      ii. Tensile testing in the presence of gaseous hydrogen under pressure various pressures
      iii. Fracture testing in the presence of gaseous hydrogen under pressure various pressures
      iv. Fatigue testing in the presence of gaseous hydrogen under pressure various pressures
2. Share and incorporate knowledge into codes and standards

Work related to barrier coatings, development of alternative alloys and financial analysis were place on hold.

Research and Development

Four commercially available pipeline steels along with two commercially available alternative steels (abrasion resistant and high strength structural steels) where selected for the original testing program. Steel samples for the six different alloys for the project along with material test reports were supplied by industry partner EVRAZ Oregon Steel Mills. The six steels, **Table 1**, were chosen based on their respective microstructural variations and in the case of the pipeline steels representation of recent commercial transmission pipeline microstructure designs. However, as stated prior focus was redirected toward working with the four commercially available pipeline steels labeled "A", "B", "C" and "D" in **Table 1**.

Table 1: Six Steels in Original DOE Project

Project/ Alloy ID	Grade	C	Comment (Perception of microstructure performance in H2 gas)
A	API X70	0.08	Baseline
B	API X70/X80	0.05	Potentially Good
C	API X70/X80	0.04	Potentially Good
D	API X60 HIC	0.03	Potentially Best
E	100 KSI Minimum Yield Strength Hot Rolled Structural Steel	0.08	Potential Alternative
F	Quench and Tempered Abrasion Resistant 400 BHN	0.15	Potential Alternative

The first step of the project was to characterize the microstructures of the six different steels in the project. This was completed through project industry partner Reference Metals Company over the timeframe of the project. Optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to identify the various microstructural phases and to estimate volume fractions of the six different steels in **Table 1**. The characterization of the microstructures for the six different steels in the project resulted in the following volume fractions:

- **Alloy A (API X70)** – 92% Polygonal Ferrite/8% Upper Bainite
- **Alloy B (API X70/X80)** – 90% Polygonal Ferrite/10% Coarse Acicular Ferrite
- **Alloy C (API X70/X80)** – 90% Polygonal Ferrite/10% Coarse Acicular Ferrite with a very small amount of Pearlite
- **Alloy D (API X60 HIC)** – 100% Polygonal Ferrite
- **Alloy E (100 KSI Minimum Yield Strength Hot Rolled Structural Steel)** – 100% Acicular Ferrite
- **Alloy F (Quench and Tempered Abrasion Resistant 400 BHN)** – 80% Acicular Ferrite/20% Lath-type Bainite

Mechanical property testing of selected project alloys (pipeline steels only as noted prior that primary focus would be on the four pipeline steels for the project) were carried out by industry partner Advanced Technology Corporation (ATC) and Oak Ridge National Laboratory (ORNL). Advanced Technology Corporation uses a patented stress-strain microprobe automated ball indentation method for determining mechanical properties of metal. ORNL used the standard ASTM E8 round bar tensile test method for mechanical property determination.

High pressure gaseous hydrogen testing capabilities were developed by ATC and ORNL. The ATC approach consisted of machining disks from steel samples and placing them in specially developed chamber that could be pressurized up to 5000 psi with gaseous hydrogen and then testing using the SSM approach over time, **Figure 1**[2]. ATC tested project alloy ID's A and D at 2000 psi hydrogen pressure for

200 hours along with industry sample of seamless pipe API X80 and an ERW pipe API Gr B. Only the seamless API X80 showed any degradation in mechanical properties when exposed to hydrogen. The fracture toughness of the seamless API X80 fracture toughness as measured by K_{JC} decreased 43% after 200 hours exposure. Strength actually increased slightly which would not be considered normal when exposed to hydrogen. Results of the four steels from the ATC SSM testing can be seen in **Figure 2**. One item that the ATC SSM hydrogen testing showed is that the degradation of fracture toughness performance happened within the first 25 hours of exposure and then leveled off after that. Additional exposure time did not seem t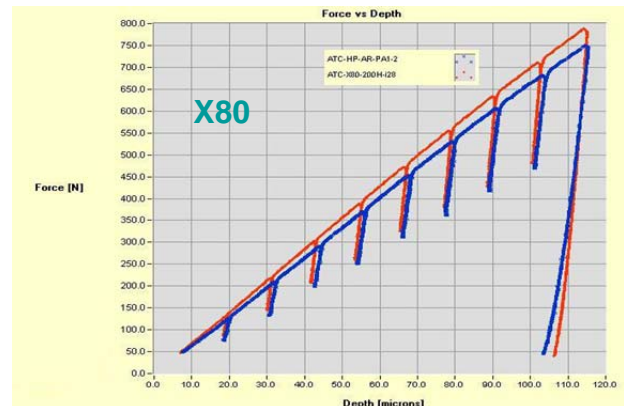o affect the remaining results. After a review of the ATC SSM testing results, it was determined by the group that this method may not be valid as an evaluation technique for the project and any additional testing was abandoned.

Fig. 1 – ATC SSM hydrogen testing apparatus. Picture on left shows set up, while picture on right shows details of pressurized hydrogen disk.

ATC SSM testing results for API Gr B ERW non-project pipeline steel. Note that both the red and blue lines are basically on top of each either signifying that the test method did not see any difference with exposure to 200 hours of 2000 psi hydrogen gas.

ATC SSM testing results for API X80 seamless non-project pipeline steel. Note that there is a separation between the red and blue lines signifying that the test method did see a difference with exposure to 200 hours of 2000 psi hydrogen gas.

ATC SSM testing results for API X60 HIC LSAW project pipeline steel. Note that both the red and blue lines are basically on top of each either signifying that the test method did not see any difference with exposure to 200 hours of 2000 psi hydrogen gas.

ATC SSM testing results for API X70 LSAW project pipeline steel. Note that both the red and blue lines are basically on top of each either signifying that the test method did not see any difference with exposure to 200 hours of 2000 psi hydrogen gas.

ATC SSM fracture toughness of API X80 seamless non-project pipeline steel results showing a 43% decrease in fracture toughness when exposed to hydrogen gas for 200 hours at 2000 psi hydrogen gas pressure.

Fig. 2 – ATC SSM Automated Ball Indentation test results in air and gaseous hydrogen for 200 hours at 2000 psi. Red lines represent air testing and blue lines represent gaseous hydrogen testing.

Ex-situ hydrogen and helium testing was carried out with partner Sandia National Laboratory – Livermore (SNLL) on project pipeline steel Alloy's A, B and C. Parameters of the ex-situ testing conducted at SNLL were as follows:
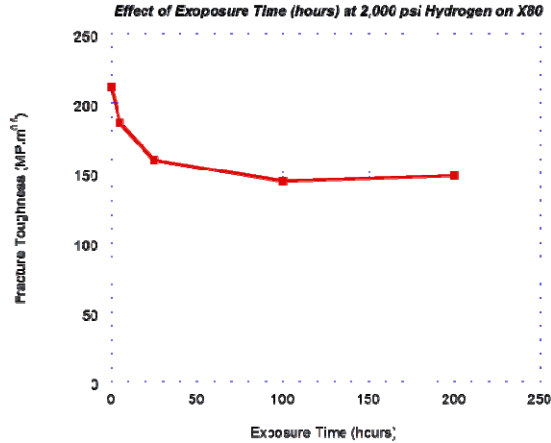
- Hydrogen testing parameters
    - Pressure – 20, 000 psi (138 MPa)
    - Temperature – 100 C
    - Duration of the testing – 8 days
    - Strain rate – 10^{-4} in/in/sec
- Helium testing parameters
    - Pressure – 5000 psi (34.5 MPa)
    - Temperature – 100 C
    - Duration of the testing – 8 days
    - Strain rate – 10^{-4} in/in/sec

The results showed that microstructure did indeed have an effect on performance with project Alloy A showing instability in the stress-strain curve and project Alloy's B and C showing stable stress-strain curves, **Figure 3**[3].

Project pipeline steel Alloy A, note the instability of the stress strain curve and degradation of strength with the exposure to hydrogen

Project pipeline steel Alloy B, note the excellent stability of the stress strain curve and no degradation of strength with the exposure to hydrogen
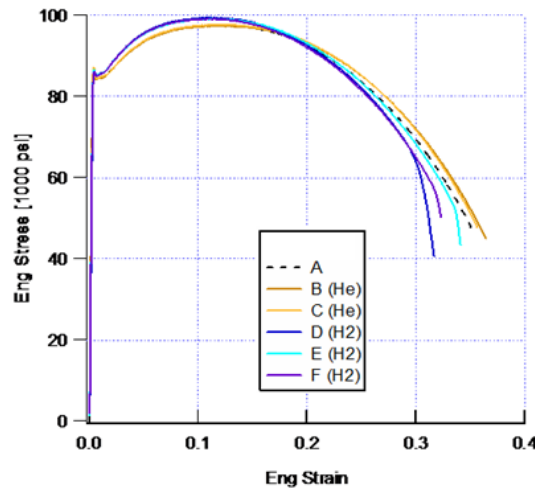
Project pipeline steel Alloy A, note the slight instability of the stress strain curve and slight degradation of strength with the exposure to hydrogen. This slight difference is most likely to the slight differences noted in microstructures between Alloy B and Alloy C.

Fig. 3 – Ex-situ hydrogen/helium testing conducted on project pipeline steel Alloy's A, B and C at SNLL

Standard NACE TM0284 Solution A (low pH) testing for resistance to hydrogen induced cracking of the four pipeline steels was conducted by industry partner EVRAZ Oregon Steel Mills. While this is a corrosive type HIC test and considered a more severe environment than a gaseous pressurized hydrogen environment absent of corrosion mechanism, it does give a relative idea of a given microstructure's resistant to hydrogen induced cracking. Regardless of how the hydrogen is introduced into the steel matrix, a microstructures ability to resist mechanical property degradation is the same. NACE TM0284 testing measures HIC resistance in the form of CLR (crack length ratio), CTR (crack thickness ratio) and CSR (crack sensitivity ratio). As expected the baseline Alloy A API X70 microstructure performed the worst in this type of testing. The other three pipeline steels (Alloy B, C and D) overall performed very well with mostly zero CLR, CTR and CSR results. The results of this testing strongly suggests that there would be microstructures that would have reasonable performance in a high pressure gaseous hydrogen environment.

ORNL developed standard round bar tensile testing capability in an autoclave vessel capable of testing in pressurized gaseous hydrogen up to 5000 psi, **Figure 4**.

Fig. 4 – ORNL high pressure hydrogen tensile testing apparatus.

Using round bar tensile specimens, ORNL tested the four pipeline steels in air and then hydrogen pressures of 1600 psi (11 MPa) and 3000 psi (20.6 MPa). These two pressures were chosen based on input from the DOE Pipeline Working Group and partner ASME through the ASME B31.12 Hydrogen Piping and Pipeline Systems codes and standards committees as being reasonable and realistic potential operating pressures for hydrogen gas transmission. Initial testing at 1600 psi in hydrogen and helium of project pipeline steels Alloy's A and C with different strain rates at ORNL showed that the presence of hydrogen had an effect on the fracture features of the tensile specimen along with decreasing the total strain required for complete failure, **Figure 5**. Alloy C seemed to perform slightly better than Alloy A in this first initial testing.
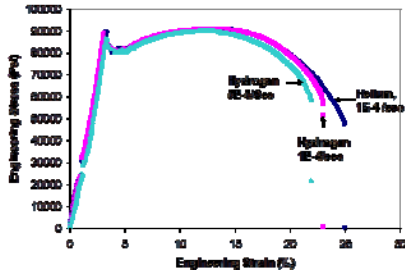
Project Alloy A API X70 pipeline steel tensile tested in hydrogen and helium at two different strain rates. Note that the presence of hydrogen decreases total strain needed for failure, regardless of strain rate.

Helium Testing - Typical Ductile cup and cone fracture

Hydrogen Testing - Faceted fracture surface with evidence for multiple secondary cracking

Project Alloy C at 10^{-4} strain rate. Note that presences of hydrogen decreases total strain to failure.

Helium Testing - Typical Ductile cup and cone fracture

Hydrogen Testing - Faceted fracture surface with evidence for multiple secondary cracking, does not seem as severe as in Alloy A

Fig. 5 – Project Alloy's A and C tensile tested at 1600 psi hydrogen and helium at ORNL

Based on this initial testing, a tensile testing matrix was developed for the four commercial pipeline steels Alloys A-D at ORNL. The details of the tensile testing matrix parameters are as follows:

- Three different test pressures (800 psi (5.5 MPa), 1600 psi (11 MPa), 3000 psi (20.7 MPa)
- Two different strain rates (10^{-4}, 10^{-5})
- Two different gas mediums (hydrogen, helium)

The results of the tensile testing revealed the following effects of hydrogen on the four different project pipeline alloys/microstructures[4]:

1. There was an initial decrease in reduction in area (RA) from testing in helium to 800 psi (5.5 MPa) hydrogen gas testing for *ALL* four alloys/microstructures and for both strain rates.
2. After the initial reduction in area decrease at 800 psi (5.5 MPa), different microstructures performed differently with increasing hydrogen pressure up to 3000 psi (20.7 MPa). Alloy B and D performing the best with increasing pressure.
3. There was no effect on actual yield and ultimate strength when exposed to hydrogen.

Figure 6 shows the results of the reduction in area tensile testing at three different hydrogen pressures and two different strain rates performed at ORNL.
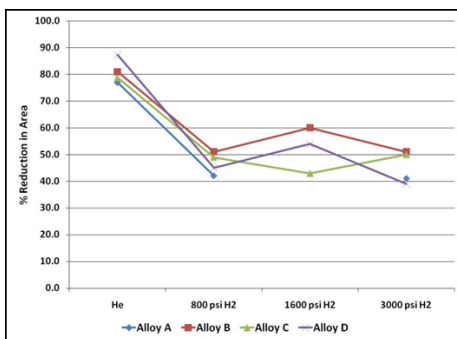
Reduction in area results four pipeline steel alloys/microstructures at 10^{-4} strain rate at various hydrogen pressures. Note the initial drop at 800 psi and then the performance with increasing pressure. Overall Alloy's B and D perform the best with increasing pressure.
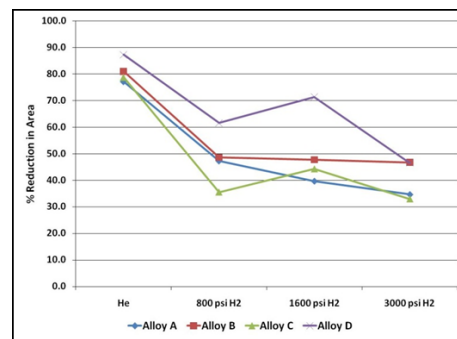
Reduction in area results four pipeline steel alloys/microstructures at 10^{-5} strain rate at various hydrogen pressures. Note the initial drop at 800 psi and then the performance with increasing pressure. Overall Alloy's B and D perform the best with increasing pressure.
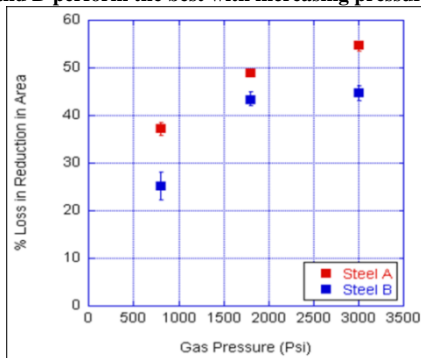
% loss in reduction in area statistics of Alloy's A and B vs. hydrogen pressure at 10^{-5} strain rate. Note the overall stability of each result at pressure
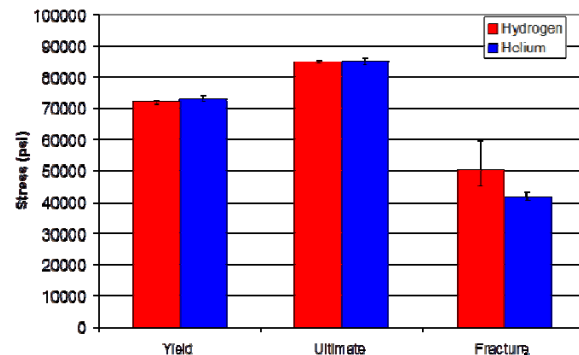
Example of strength changes for Alloy B in hydrogen vs. helium at 10^{-5} strain rate. There is no effect on yield or ultimate strength only fracture stress in the presence of hydrogen.

Fig. 6 – Results of hydrogen/helium tensile testing at ORNL

Based on the results of the ORNL testing and direction from the DOE Pipeline Working Group and driven by available funding, the two best performing alloys/microstructures from the ORNL tensile testing, Alloy's B and D were chosen for further testing[5]. The DOE Pipeline Working Group direction was to further test for fracture toughness and fatigue performance. Due to the type of hydrogen testing capability required for fracture toughness and fatigue testing project partner Sandia National Laboratory – Livermore was enlisted for this phase of the project. SNLL has the necessary equipment and expertise to perform high pressure gaseous hydrogen fracture toughness and fatigue testing. Fracture toughness testing at SNLL was funded out of the original DOE project funding through a work for others agreement. Fatigue testing at SNLL was funded by project industry partner Reference Metals Company also through a work for others agreement. The SNLL fracture toughness and fatigue testing was conducted at 800 psi and 3000 psi. These two pressures were chosen with input from the project partner ASME and more importantly input from ASME B31.12 Hydrogen Piping and Pipelines codes and standards committee. The two pressures would represent what would most likely be potential hydrogen transmission pipeline operating pressures.

The two project alloys chosen for the further evaluation at SNLL were Alloy's B and D. Alloy B was an API X70/X80 steel grade consisting of a microstructure of 90% polygonal ferrite/10% coarse acicular ferrite. Alloy D was an API X60 HIC steel grade consisting of a microstructure of 100% polygonal ferrite. In the fracture toughness testing, both alloys performed reasonably well with K_{JQ} values of 85-90 MPa – m$^{1/2}$ for Alloy D and 115-125 MPa-m$^{1/2}$ for Alloy B at the two pressures, **Figure 7**.
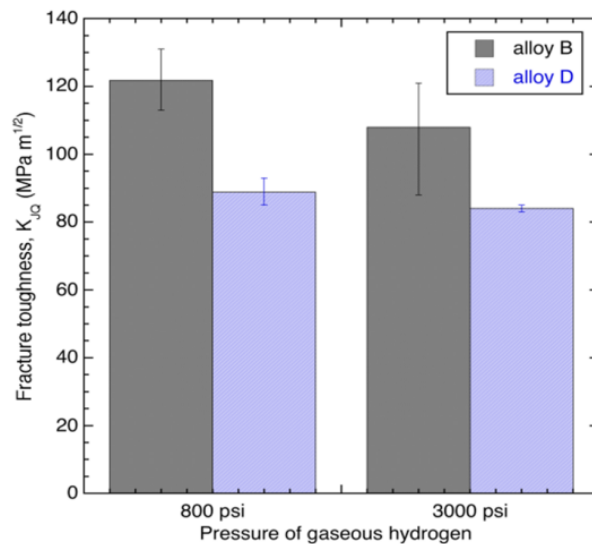
Fig. 7 – SNLL fracture toughness results at 800 psi and 3000 psi gaseous hydrogen pressure of project Alloy's B and D

SNLL, under a work for others agreement with funding through project partner Reference Metals Company, conducted fatigue testing utilizing two R-ratio values (0.5 and 0.1, R is the ratio of the minimum to maximum load applied to the specimen) on Alloy's B and D at 800 and 3000 psi (5.5 and 21 MPa). In addition, testing was completed in air for both alloys for comparison. There was no significant difference in fatigue results by R-ratio values or microstructures. However, both microstructures showed tendencies of convergence with those values generated in air at lower ΔK values, **Figure 8**.

Measured Fatigue Crack Growth Rate in Hydrogen (800 and 3000 psi) and Air of Alloy B at two R-values

Measured Fatigue Crack Growth Rate in Hydrogen (800 and 3000 psi) and Air of Alloy D at two R-values

Fig. 8 – SNLL fatigue testing of project Alloy's B and D

The fracture toughness and fatigue testing of project Alloy's B and D concluded the available funding for the original DOE funded project. However, as this information was shared with industry and ASME codes and standards enough interest was generated to continue the work on the original project Alloy A while expanding the testing program to and additional ten different alloy/microstructure/processing of pipeline steels covering alloy/microstructure designs for transmission pipelines from the 1960's to 2010. Since fracture and fatigue results were of the most interest to those within the DOE Pipeline Working Group and ASME B31.12 Piping and Pipelines codes and standards committee, this would be the focus of this "Phase 2" research. The total package of research was covered under private sector funding from ASME and Reference Metals Company along with US DOT funding at SNLL and NIST. **Figure 9** shows the total matrix of fracture and fatigue testing that has been completed or is in progress to be completed that developed from this original DOE funded research work. Yellow highlighting in the figure shows the original six alloys/microstructures with the orange highlighted areas showing the fracture and fatigue t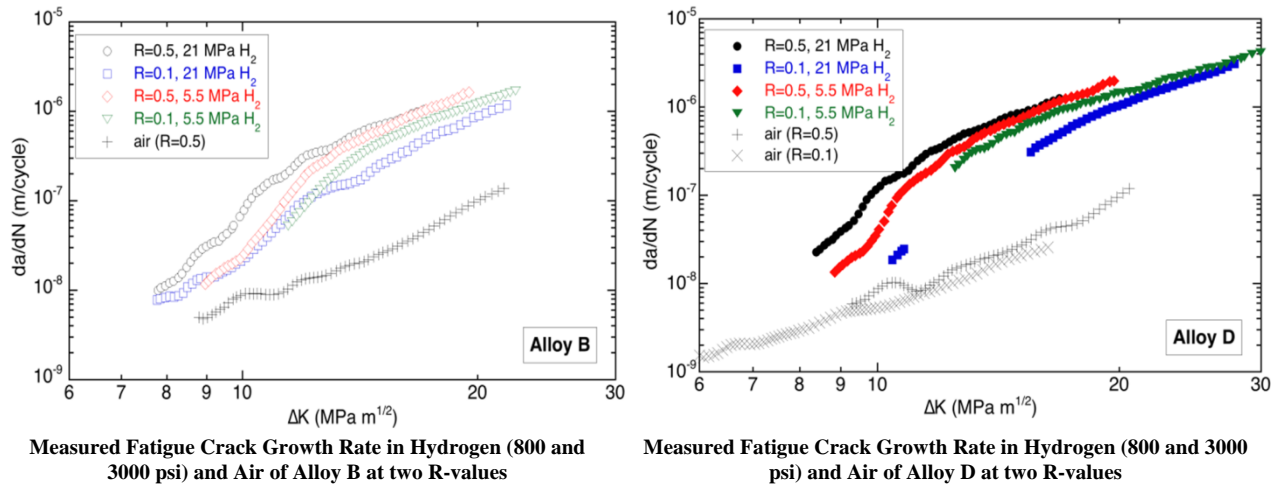esting concluded with the original DOE funding plus some private sector funding. Blue and green shaded areas shows testing either completed or in progress funded through additional private sector funding along with DOT funding. As can be seen a significant number of alloy/microstructure designs, including one pressure vessel steel, have been or are in the process of being evaluated that would cover a wide range of possible alloy/microstructure designs in North America from the 1960's in the Phase 2 testing program. Included in this testing was induction bend pipe to evaluate the effect of the induction bending operation. The white highlighted/not tested are alloys/microstructures where there is not a significant amount of interest or no available funding to complete the testing (i.e. – seam/girth welds are areas of interest but no funding availability).

Item	Project Code	Grade	Microstructure	Fracture Test 800 psi Location (2 samples)	Fracture Test 3000 psi Location (2 Samples)	Fatigue Testing 800 psi Location (2 samples)	Fatigue Testing 3000 psi Location (2 samples)
1	A	API - Late 1990's X70 Design	92% PF/8% UB	Completed - Report Written***	Completed - Report Written***	In-progress - NIST	In-progess - NIST
2	B	API - 2000's X70/X80 w/o Moly Design, Lo Cr	90% PF/10% CAF	Completed*	Completed*	Completed*	Completed*
3	C	API - 2000's X70/X80 w/o Moly Design, Hi Cr	90% PF/10% CAF+ Sm UB	Not Tested	Not Tested	Not Tested	Not Tested
4	D	API - Current X60 HIC Design	100% PF	Completed*	Completed*	Completed*	Completed*
5	Secat E	Structural 100 KSI Design	100% AF	Not Tested	Not Tested	Not Tested	Not Tested
6	Secat F	400 BHN Abrasion Resistant Design	80% AF/20% Lath Type Bainite	Not Tested	Not Tested	Not Tested	Not Tested
7	Sandia E	API - 2000's X70/X80 w Moly Design	100% FAF	Completed - Report Written***	Completed**	In-progress - NIST	Completed**
8	Sandia F	API - 2000's X70/X80 w/o Moly Design	30% PF/70% FAF	Completed - Report Written***	Completed**	In-progress -NIST	In-progress - NIST
9	G	API - 1980's X70 Alloy Design	90% PF/10% P	Completed - Report Written***	Completed - Report Written***	In-progress -NIST	In-progress - NIST
10	H	API - 1960's X52 Alloy Design	70% PF/30% P	Completed - Report Written***	Completed - Report Written***	In-progress -NIST	In-progress - NIST
11	I	API - Early 1990's X70 Design	85% PF/15% P	Completed - Report Written***	Completed - Report Written***	In-progress - NIST	In-progress - NIST
12	J	API - 1990's/2000's X52 Alloy Design	92% PF/5% AF/3% P	Completed - Report Written***	Completed	In-progess - NIST	Completed
13	K	PV - ASTM A516 Gr70 w/o microalloy	PF/P (40+%) TBD	Not Tested	Not Tested	Not Tested	Not Tested
14	L	PV - ASTM A516 Gr70 with microalloy	40% PF/60% P	Completed - Report Written***	Completed - Report Written***	Not Tested	Not Tested
15	M	API X70 - Pipeline Long Seam Welds	As-castTBD	Not Tested	Not Tested	Not Tested	Not Tested
16	N	API - Pipeline Girth Welds	As-castTBD	Not Tested	Not Tested	Not Tested	Not Tested
18	P Ind	Induction Bend Comparison X52	95% PF/5% AF	Completed - Report Written***	Completed - Report Written***	In-progress -NIST	In-progress - NIST
19	P Nind	Non-Induction Bend Comparison X52	90% PF/10% AF	Completed - Report Written***	Completed - Report Written***	In-progess - NIST	In-progess - NIST

Fig. 9 – Matrix of original DOE funded fracture/fatigue testing plus "Phase 2" fracture/fatigue testing from additional private sector/DOT funding.

Technology Transfer

During the entire project as data was being generated along with the additional information generated in the non-DOE funded "Phase 2" program, the testing parameters and results have been shared with various organizations/team members. Presentations have been made at each US DOE Annual Peer Review Meeting, at each DOE Pipeline Working Group meeting, paper/presentations at ASME PVP 2009, 2010, 2011 and the upcoming 2013 conferences, ASME International Pipeline Conferences in 2010 and 2012, 2008 and 2012 International Hydrogen Conference and with the ASME B31.12 Piping and Pipelines codes and standards committee. Project partner DGS Metallurgical Solutions, Inc. is a member of the ASME B31.12 codes and standards committee and is working with the committee to make guidance language modifications to the existing B31.12 code based on the results of the work from the original DOE funded project and additional "Phase 2" work. The ASME B31.12 committee has representation from three large industrial hydrogen producers which have access to the data generated by the initial program and the "Phase 2" program demonstrating the importance of proper microstructure selection in optimizing the design of hydrogen piping and pipeline systems.

Summary, Conclusions and Recommendations

This originally funded DOE work coupled with the additional Phase 2 work has significantly increased the understanding of the role of steel alloy designs, microstructures and mechanical property performance when exposed to gaseous hydrogen in the pressure ranges of 800 – 3000 psi. Even though there is mechanical property degradation with initial exposure to hydrogen for all steels evaluated, mechanical property performance of certain microstructures can become stable with increasing hydrogen pressure. Mechanical property performance of certain microstructures may be more than adequate to perform safely for hydrogen gas service applications. This strongly implies that pipeline steels that exist in some of the current North American transmission pipeline infrastructure may be suitable for gaseous hydrogen transportation. It also strongly suggests that current pipeline steel technology can be used to develop microstructures that have suitable mechanical properties in the presence of gaseous hydrogen in pressures up to 3000 psi.

From this original DOE funded work the following conclusions can be made:

1. Pipeline steel microstructures evaluated in the project all experienced an initial degradation in mechanical properties with initial exposure to hydrogen gas under pressure (800 psi) as measured by reduction in area tensile testing.
2. However, once the initial degradation was reached, microstructures behaved differently with continued increasing hydrogen pressure up to 3000 psi.
3. Microstructures of polygonal ferrite and/or acicular ferrite with no presence of upper bainite or pearlite performed the best in hydrogen pressures up to 3000 psi as measured by reduction in area tensile testing.
4. Absolute yield and ultimate strength were not affected by exposure to hydrogen; only the stress to final fracture was affected by hydrogen.
5. Fracture toughness varied by microstructure with slight decreases in toughness with increasing hydrogen pressure for each of the two microstructures tested.
6. Fatigue testing between the two microstructures with two different frequencies and pressures showed no significant difference when exposed to hydrogen.
7. Since fatigue was not significant between the two microstructures then microstructure design to optimize fracture toughness can be considered. A polygonal ferrite/acicular ferrite microstructure generated the highest fracture toughness values up to 3000 psi of the two microstructures evaluated.
8. Increasing yield strength did not affect the fracture toughness performance in hydrogen up to 3000 psi as has been reported previously by others.
9. Even though the polygonal ferrite/acicular ferrite microstructure performed the best in this evaluation, this does not necessarily mean that some of the other microstructures are not suitable for hydrogen service. Suitability will have to be determined by the requirements of the

Based on the project work, the following recommendations can be made:

1. Correlations need to be developed between the fracture toughness/fatigue test results with those of a more traditional steel testing technique such as the V-notch Charpy toughness testing. The standard steel testing protocol then can be used in developing specifications.
2. Additional steel microstructures have been evaluated for fracture toughness since this original project, however, as illustrated in **Figure 9** there are still additional alloys/microstructures and probably a few more added to the matrix (X70 induction bend pipe as an example) that should be evaluated.
3. Fatigue testing needs to be completed as illustrated in the **Figure 9** matrix.

4. Various seam and girth welds need to be evaluated at 800 and 3000 psi. This includes submerged arc welded material along with other field welding techniques and consumable combinations.
5. Based on this work along with the additional work done in Phase 2, a clearer picture is developing of what an optimum metallurgical/alloy/microstructure hydrogen transmission pipeline may look like. A small (30-35 pipe lengths of a standard 40 feet length) rectangular demonstration pipeline should be built complete with a compressor station and monitoring equipment based on current knowledge and understanding. This line could be built and monitored at a national laboratory site such as Sandia National Laboratory – Livermore.

Project Discussion

Background

The continued growth of the world's developing countries has placed an ever increasing demand on traditional fossil fuels. This increased demand for fossil fuels has led to increasing research and development of alternative energy sources. Hydrogen gas is one of the potential alternatives under development. It is anticipated that the least expensive method of transporting large quantities of hydrogen gas is through steel pipelines. It is well known that hydrogen embrittlement has the potential to degrade steel's mechanical properties. Consequently, the current pipeline infrastructure used in hydrogen transport is typically operated in a conservative fashion, in particular lower operating pressures, lower strength steels, and heavier pipe wall thicknesses. This operational practice is not conducive to economical movement of significant volumes of hydrogen gas as an alternative to fossil fuels.

The degradation of the mechanical properties of steels in hydrogen service depends on the microstructure of the steel. An understanding of the relationship of mechanical property degradation of a given microstructure on exposure to hydrogen gas under pressure can be used to evaluate the suitability of the existing pipeline infrastructure for hydrogen service and guide alloy and microstructure design for new hydrogen pipeline infrastructure. To this end, the microstructures of relevant steels and their mechanical properties in relevant gaseous hydrogen environments must be fully characterized to establish suitability for transporting hydrogen.

A project to evaluate four commercially available pipeline steels alloy/microstructure performance in the presences of gaseous hydrogen has been funded by the US Department of Energy along with the private sector. The microstructures of four pipeline steels were characterized and tensile testing was conducted in gaseous hydrogen and helium at pressures of 5.5 MPa (800 psi), 11 MPa (1600 psi) and 20.7 MPa (3000 psi). Based on reduction of area, two of the four steels that performed the best across the pressure range were selected for evaluation of fracture and fatigue performance in gaseous hydrogen at 5.5 MPa (800 psi) and 20.7 MPa (3000 psi).

Introduction

For both economic and environmental reasons, alternative energy sources to fossil fuels need to be developed. One potential energy source for the transportation sector is hydrogen gas. The US Department of Energy, over the past several years, has been funding research and development efforts in both fuel cell technology and hydrogen delivery systems. On the delivery side of the hydrogen as a fuel source equation, the most economical method to move large volumes of gas is through a pipeline infrastructure.

The majority of today's pipeline infrastructure is made of steel. Degradation of the mechanical properties of the steel is always a concern when exposed to hydrogen gas. To address this concern a project funded by both the DOE and the private sector has been evaluating commercial grade pipeline steels' performance in the presence of pressurized hydrogen gas. The project is coordinated by Secat, Inc. with key partners from the private/industrial sector: University of Illinois, Oak Ridge National Laboratory, Oak Ridge, TN, Reference Metals Company, Pittsburgh, PA, Sandia National Laboratory, Livermore, CA, and DGS Metallurgical Solutions, Inc in Vancouver, WA.

The main objective of the study is as follows: ***Identify steel compositions/microstructures suitable for construction of new pipeline infrastructure and evaluate the potential use of the existing steel pipeline infrastructure in high pressure gaseous hydrogen applications.***

To address the objective, four commercially available pipeline steels along with two commercially available structural steels were selected for evaluation. The selection of the six steels was based on the expected performance of each microstructure in the presence of gaseous hydrogen. It is known from the literature and experiences that microstructure along with internal steel cleanliness of the alloy play a major role in the interaction of hydrogen in the matrix and subsequent mechanical property performance[6,7]. A general description of each alloy selected can be found in **Table 2**. The comments in the table are in regard to the expected performance of each grade go the presence of gaseous hydrogen under pressure and are based on the perception of microstructure and performance experiences in a NACE TM0284 corrosion hydrogen environment. Final microstructural verification was part of the project evaluation and will be presented in a later section.

Table 2: Six Steels in Original DOE Project

Project ID	Grade	C	Comment (Perception of microstructure performance in H_2 gas)
A	API X70	0.08	Baseline
B	API X70/X80	0.05	Potentially Good
C	API X70/X80	0.04	Potentially Good
D	API X60 HIC	0.03	Potentially Best
E	100 KSI Hot Rolled Structural Steel	0.08	Potential Alternative
F	Abrasion Resistant 400 BHN	0.15	Potential Alternative

Details of chemistry and microstructural characterization of the four pipeline steels can be seen in **Table 3**.

Table 3: Details of Six Commercial Grade Steels to be evaluated in Hydrogen Study

Project ID	Grade	C	Mn	P	S	Nb	V	Other	Microstructure
A	API X70	0.08	1.61	0.010	0.002	0.061	0.050	Si, Ti ≤0.29	92% Polygonal Ferrite/8% Upper Bainite
B	API X70/X80	0.05	1.52	0.007	0.003	0.092	0.001	Si, Cu, Ni, Cr, Ti ≤0.75	90% Polygonal Ferrite/10% Coarse Acicular Ferrite
C	API X70/X80	0.04	1.61	0.010	0.002	0.096	0.001	Si, Cu, Ni, Cr, Ti ≤0.92	90% Polygonal Ferrite/10% Coarse Acicular Ferrite with a very small amount of Pearlite
D	API X60 HIC	0.03	1.14	0.008	0.001	0.084	NIA	Si, Cu, Ni, Cr, Ti ≤0.73	100% Polygonal Ferrite
E	100 KSI Hot Rolled Structural Steel	0.08	1.71	0.011	0.005	0.044	NIA	Si, Ni, Ti, B ≤0.93	100% Acicular Ferrite
F	Abrasion Resistant 400 BHN	0.15	1.42	0.014	0.004	0.014	NIA	Si, Cr, Mo, Ti, B ≤1.00	80% Acicular Ferrite/20% Lath-type Bainite

After discussions and input from the DOE Hydrogen Project Management and DOE Pipeline Working Group it was decided that with available funding the focus of the project would only be on the four commercially available transmission pipeline steels, Project ID's A-D in **Table 3**.

The basic format for this phase of the study is as follows:

- Microstructural characterization of volume fraction of phases in each alloy
- Tensile testing of all four alloys in He and H_2 at 5.5 MPa (800 psi), 11 MPa (1600 psi), and 20.7 MPa (3000 psi). RA performance was used to choose the two best performers for further mechanical property evaluation.
- Fracture testing (ASTM E1820) of two best tensile test performers in H_2 at 5.5 MPa (800 psi) and 20.7 MPa (3000 psi).
- Fatigue testing (ASTM E647) of two best tensile test performers in H_2 at 5.5 MPa (800 psi) and 20.7 MPa (3000 psi) with frequency =1.0 Hz and R-ratio=0.5 and 0.1.

In the results section of the paper, the project codes Alloy A, B, C, and D are used to identify the four steels that were evaluated.

Initial Hydrogen Testing at ATC, ORNL and SNLL

High pressure gaseous hydrogen testing capabilities were developed by ATC and ORNL. The ATC approach consisted of machining disks from steel samples and placing them in specially developed chamber that could be pressurized up to 5000 psi with gaseous hydrogen and then testing using the SSM approach over time, **Figure 10**. ATC tested project alloy ID's A and D at 2000 psi hydrogen pressure for 200 hours along with industry sample of seamless pipe API X80 and an ERW pipe API Gr B. Only the seamless API X80 showed any degradation in mechanical properties when exposed to hydrogen. The fracture toughness of the seamless API X80 fracture toughness as measured by K_{JC} decreased 43% after 200 hours exposure. Strength actually increased slightly which would not be considered normal when exposed to hydrogen. Results of the four steels from the ATC SSM testing can be seen in **Figure 11**. One item that the ATC SSM hydrogen testing showed is that the degradation of fracture toughness performance happened within the first 25 hours of exposure and then leveled off after that. Additional exposure time did not seem to affect the remaining results. After a review of the ATC SSM testing results, it was determined by the group that this method may not be valid as an evaluation technique for the project and any additional testing was abandoned.
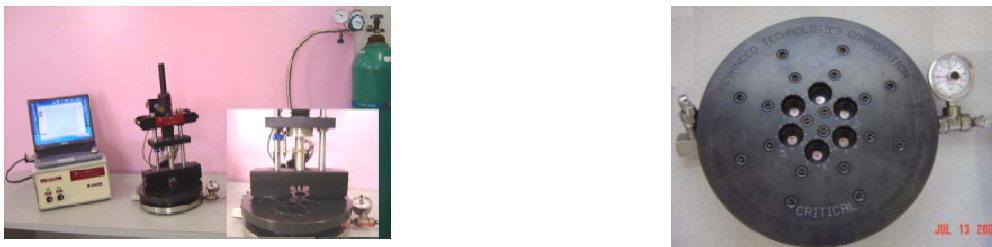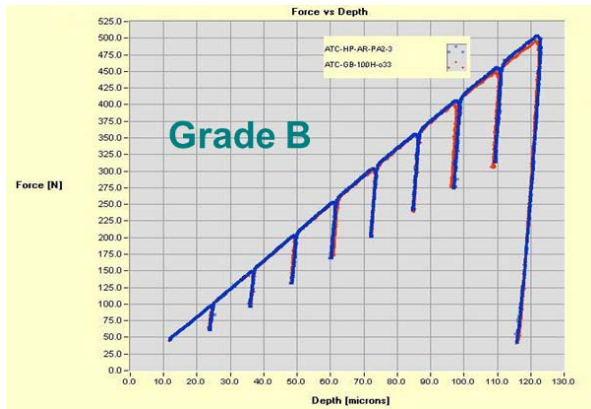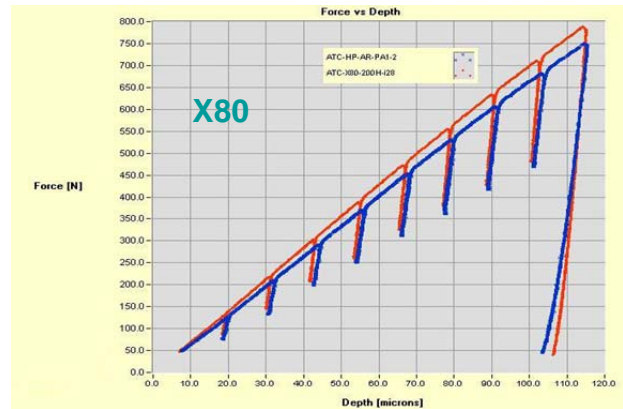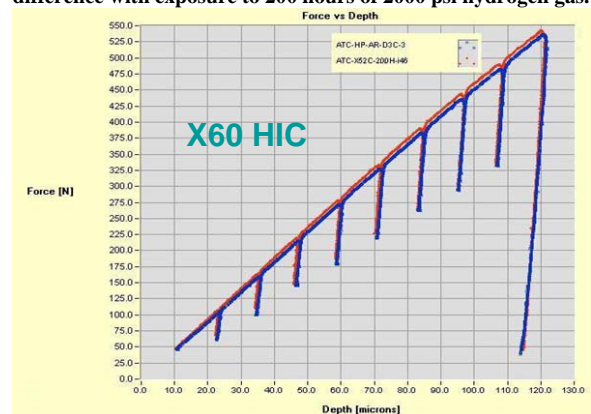

Fig. 10 – ATC SSM hydrogen testing apparatus. Picture on left shows set up, while picture on right shows details of pressurized hydrogen disk.
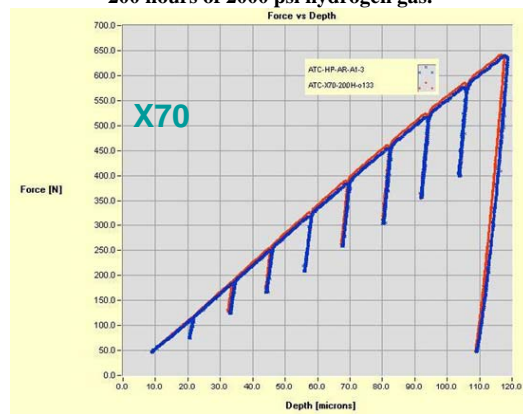
ATC SSM testing results for API Gr B ERW non-project pipeline steel. Note that both the red and blue lines are basically on top of each either signifying that the test method did not see any difference with exposure to 200 hours of 2000 psi hydrogen gas.
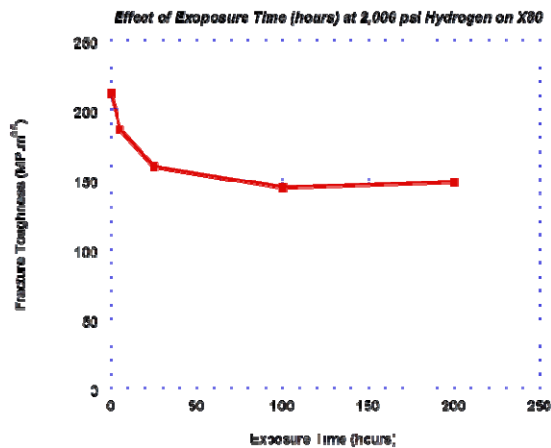

ATC SSM testing results for API X80 seamless non-project pipeline steel. Note that there is a separation between the red and blue lines signifying that the test method did see a difference with exposure to 200 hours of 2000 psi hydrogen gas.

ATC SSM testing results for API X60 HIC LSAW project pipeline steel. Note that both the red and blue lines are basically on top of each either signifying that the test method did not see any difference with exposure to 200 hours of 2000 psi hydrogen gas.

ATC SSM testing results for API X70 LSAW project pipeline steel. Note that both the red and blue lines are basically on top of each either signifying that the test method did not see any difference with exposure to 200 hours of 2000 psi hydrogen gas.
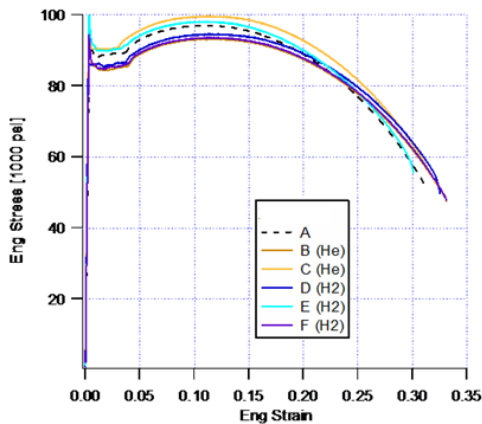

ATC SSM fracture toughness of API X80 seamless non-project pipeline steel results showing a 43% decrease in fracture toughness when exposed to hydrogen gas for 200 hours at 2000 psi hydrogen gas pressure.

Fig. 11 – ATC SSM Automated Ball Indentation test results in air and gaseous hydrogen for 200 hours at 2000 psi. Red lines represent air testing and blue lines represent gaseous hydrogen testing.
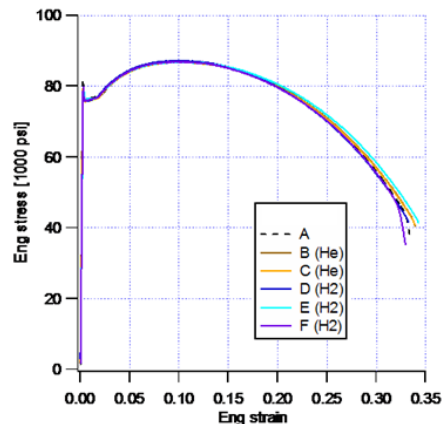
Ex-situ hydrogen and helium testing was carried out with partner Sandia National Laboratory – Livermore (SNLL) on project pipeline steel Alloy's A, B and C. Parameters of the ex-situ testing conducted at SNLL were as follows:

- Hydrogen testing parameters
  - Pressure – 20, 000 psi (138 MPa)
  - Temperature – 100 C
  - Duration of the testing – 8 days
  - Strain rate – 10^{-4} in/in/sec
- Helium testing parameters
  - Pressure – 5000 psi (34.5 MPa)
  - Temperature – 100 C
  - Duration of the testing – 8 days
 - Strain rate – 10^{-4} in/in/sec

The results showed that microstructure did indeed have an effect on performance with project Alloy A showing instability in the stress-strain curve and project Alloy's B and C showing stable stress-strain curves, **Figure 12**.

Project pipeline steel Alloy A, note the instability of the stress strain curve and degradation of strength with the exposure to hydrogen

Project pipeline steel Alloy B, note the excellent stability of the stress strain curve and no degradation of strength with the exposure to hydrogen
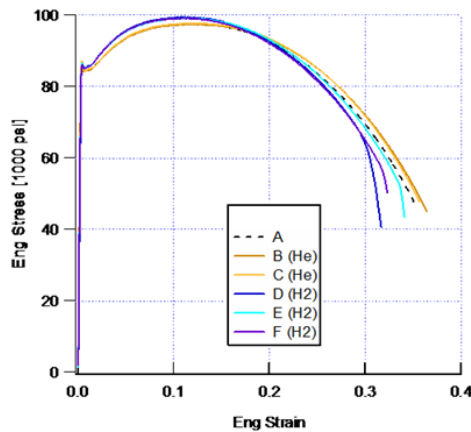
Project pipeline steel Alloy A, note the slight instability of the stress strain curve and slight degradation of strength with the exposure to hydrogen. This slight difference is most likely to the slight differences noted in microstructures between Alloy B and Alloy C.

Fig. 12 – Ex-situ hydrogen/helium testing conducted on project pipeline steel Alloy's A, B and C at SNLL

Standard NACE TM0284 Solution A (low pH) testing for resistance to hydrogen induced cracking of the four pipeline steels was conducted by industry partner EVRAZ Oregon Steel Mills. While this is a corrosive type HIC test and considered a more severe environment than a gaseous pressurized hydrogen environment absent of corrosion mechanism, it does give a relative idea of a given microstructure's resistant to hydrogen induced cracking. Regardless of how the hydrogen is introduced into the steel matrix, a microstructures ability to resist mechanical property degradation is the same. NACE TM0284 testing measures HIC resistance in the form of CLR (crack length ratio), CTR (crack thickness ratio) and CSR (crack sensitivity ratio). As expected the baseline Alloy A API X70 microstructure performed the worst in this type of testing. The other three pipeline steels (Alloy B, C and D) overall performed very well with mostly zero CLR, CTR and CSR results. The results of this testing strongly suggests that there would be microstructures that would have reasonable performance in a high pressure gaseous hydrogen environment.

ORNL developed standard round bar tensile testing capability in an autoclave vessel capable of testing in pressurized gaseous hydrogen up to 5000 psi, **Figure 13**.
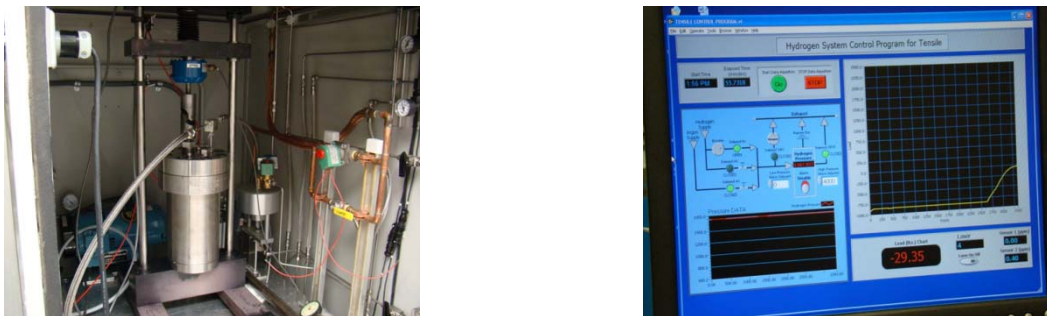

Fig. 13 – ORNL high pressure hydrogen tensile testing apparatus.

Using round bar tensile specimens, ORNL tested the four pipeline steels in air and then hydrogen pressures of 1600 psi (11 MPa) and 3000 psi (20.6 MPa). These two pressures were chosen based on input from the DOE Pipeline Working Group and partner ASME through the ASME B31.12 Hydrogen Piping and Pipeline Systems codes and standards committees as being reasonable and realistic potential operating pressures for hydrogen gas transmission. Initial testing at 1600 psi in hydrogen and helium of project pipeline steels Alloy's A and C with different strain rates at ORNL showed that the presence of hydrogen had an effect on the fracture features of the tensile specimen along with decreasing the total strain required for complete failure, **Figure 14**. Alloy C seemed to perform slightly better than Alloy A in this first initial testing.
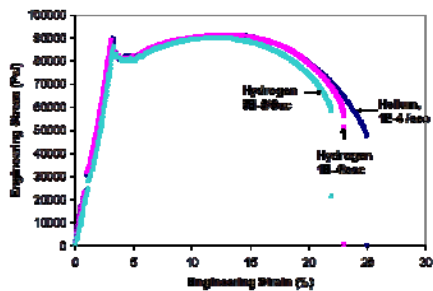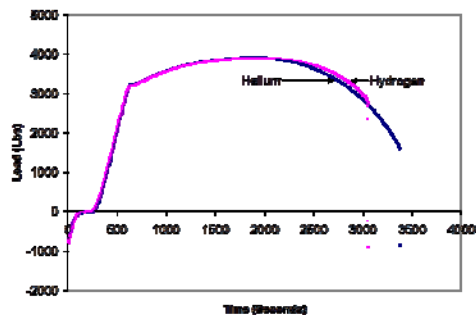

Project Alloy A API X70 pipeline steel tensile tested in hydrogen and helium at two different strain rates. Note that the presence of hydrogen decreases total strain needed for failure, regardless of strain rate.

Helium Testing - Typical Ductile cup and cone fracture

Hydrogen Testing - Faceted fracture surface with evidence for multiple secondary cracking

Project Alloy C at 10^{-4} strain rate. Note that presences of hydrogen decreases total strain to failure.	Helium Testing - Typical Ductile cup and cone fracture	Hydrogen Testing - Faceted fracture surface with evidence for multiple secondary cracking, does not seem as severe as in Alloy A

Fig. 14 – Project Alloy's A and C tensile tested at 1600 psi hydrogen and helium at ORNL

Results – As-received Compositions, Mechanical Properties, Expected Microstructure and NACE TM0284 Testing

The four pipeline steels represent typical API grades that would be used in commercial pipeline applications in the 1990's and 2000's. Alloy A is a typical API X70, C-Mn-Si-Nb-V alloy design produced by Thermomechanical Control Processing (TMCP) rolling finishing below the Ar_3 followed by air cooling. Alloy's B and C are a current X80 type alloy design used around the world utilizing an alloy design of C-Mn-Si-Nb (0.080-0.10% Nb) produced by TMCP rolling finishing above the Ar_3 followed by ACC (water) cooling. Alloy D is a low C-Mn-Si-Nb API X60 HIC designed for low pH sour service natural gas applications where resistance to hydrogen induced cracking in a NACE TM0284 low pH (Solution A) environment is expected. Alloy D was produced by TMCP rolling finishing at approximately the Ar_3 followed by air cooling. As noted in **Table 2**, Alloy A is considered a baseline grade as it is very common alloy design that has been used extensively in the past years for oil and gas transmission pipeline infrastructure. Details of the chemistry of the four as-received pipeline steels can be found in previous **Table 3**.

The as-received mechanical properties as reported by the mill producer of the four pipeline alloys can be found in **Table 4**.

Table 4: As-received Mechanical Properties of Four Pipeline Steels in the Project

Alloy	YS (MPa)	TS (MPa)	%Elongation 50 mm	YT Ratio
A	565	606	40	0.93
B	541	596	40	0.91
C	545	648	45	0.84
D	435	486	42	0.90

It should be noted that all of the samples came from plate or coil (skelp) that was destined for pipe production. The as-received strength reported is based on the expected skelp to pipe strength shifts that typically occur. Hence, Alloy A which was destined for X70 has plate YS high enough to account for the expected shift downward in YS during pipe production. In addition, Alloy's B and C were destined for X80 pipe and hence have slightly lower YS to account for an expected upward shift in YS during pipe production.

The expected microstructures of the four as-received alloy designs based on the composition and rolling design were as follows:

Alloy A – Ferrite/Pearlite (F/P)
Alloy B, C, D – Ferrite/Fine Acicular Ferrite (F/FAF*)
*Fine acicular ferrite is low carbon bainitic structure.

Microstructural characterization, which will be presented later, showed that there were differences between the actual microstructures and that expected for some of the alloys. Even though there were differences between the actual vs. expected microstructures for some of the alloys, these microstructures are valid for what might be produced in a steel production environment.

To gain a baseline understanding of the performance of the four alloys/microstructures in the presence of hydrogen, all four were tested in the NACE TM0284[8] low pH (Solution A) environment. Granted that this is a corrosion test and probably more severe than that of a gaseous hydrogen environment, once the hydrogen enters the steel matrix the performance of each microstructure in the presence of hydrogen can be compared relative to each other. The results of the NACE testing can be found in **Table 5**[9].

Table 5: Results of NACE TM0284 Low pH (Solution A) Testing of Selected Alloys

| Alloy	CLR %	CSR %	CTR %
A	11.8[a]	0	0.1
B	0.4[b]	0	0
C	0	0	0
D	0	0	0

a) **Cracks located at ferrite/pearlite interface**
b) **Cracks located between surface and ¼ thickness and associated with cluster of non-metallic inclusions (related to ¼ thickness casting inclusion issue)**

Overall, the results for each of the alloys in this corrosive environment performed as expected. Alloy A performed the worst of the four and the remaining three alloys performed about the same. If Alloy B did not have the cluster of non-metallic inclusions, its performance would have been the same as Alloys C and D. Non-metallic inclusions can act as traps for hydrogen and cause hydrogen induced cracking.

Microstructural Characterization

Microstructure plays a role in a given steel's ability to perform in the presence of hydrogen. Since the objective of this project was to identify steel compositions/microstructures that might be suitable for the transport of gaseous hydrogen under pressure, volume fraction of the microstructural phases for each alloy was determined. Optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques were used to identify major microstructural phases and to estimate the volume fraction of each phase.

Alloy A, a standard API X70, C-Mn-Si-Nb-V alloy design, was characterized as approximately 92% polygonal ferrite and 8% upper bainite[10]. Optical microscopy, SEM and TEM analysis can be seen in **Figures 15, 16 and 17,** respectively. Under the optical microscope, the upper bainite appears dark, as it has low reflectivity. At higher magnifications under SEM and TEM examination, upper bainite will exhibit a "feather-like" arrangement (**Figure 16 and 17**) of its ferrite laths in contrast to the sheaves of approximately parallel laths that one observes in pearlite or lath martensite.
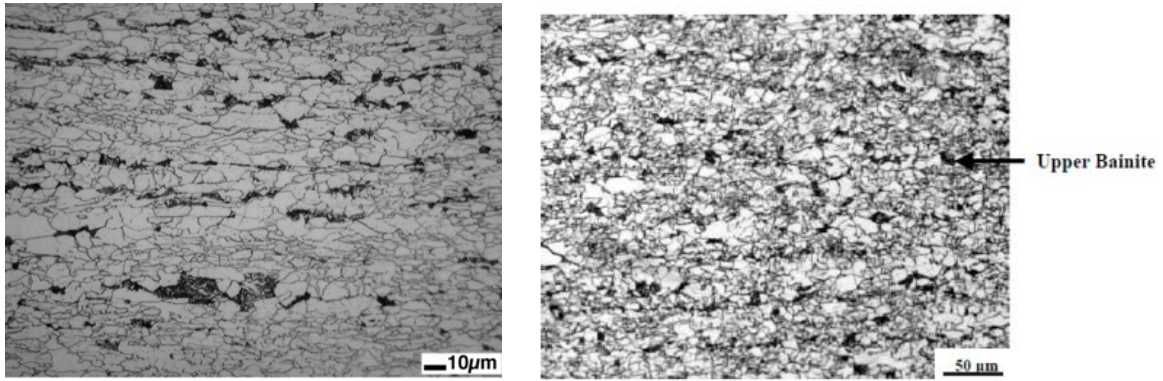
Dark Islands Identified as Upper Bainite
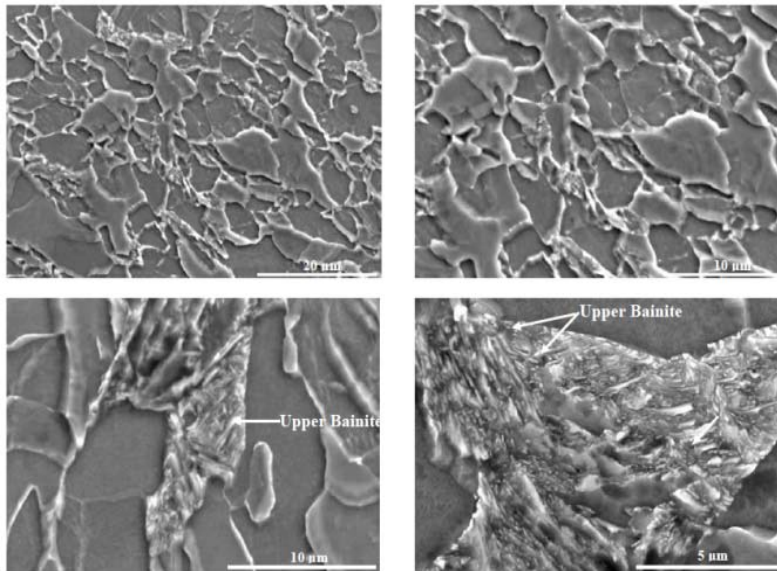**Fig. 15 - Optical microscopy characterization of Alloy A**
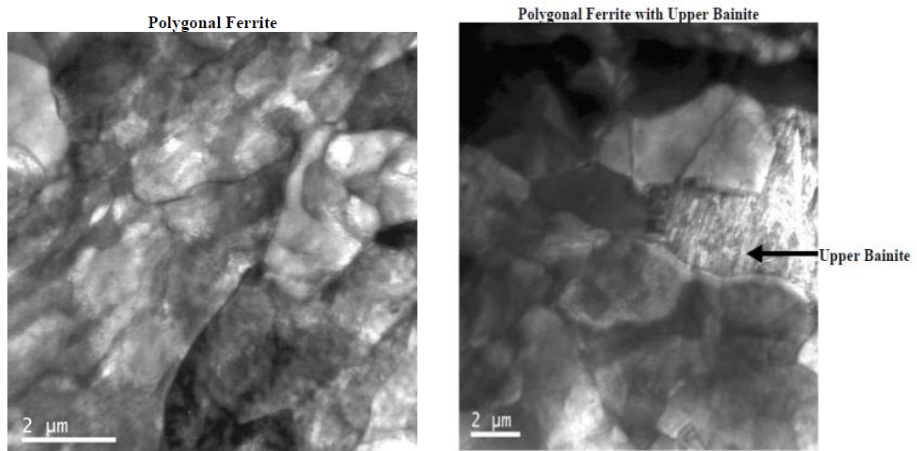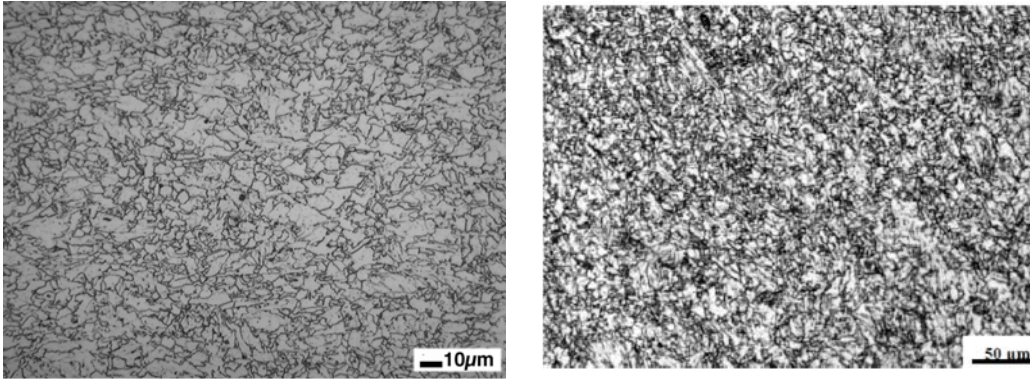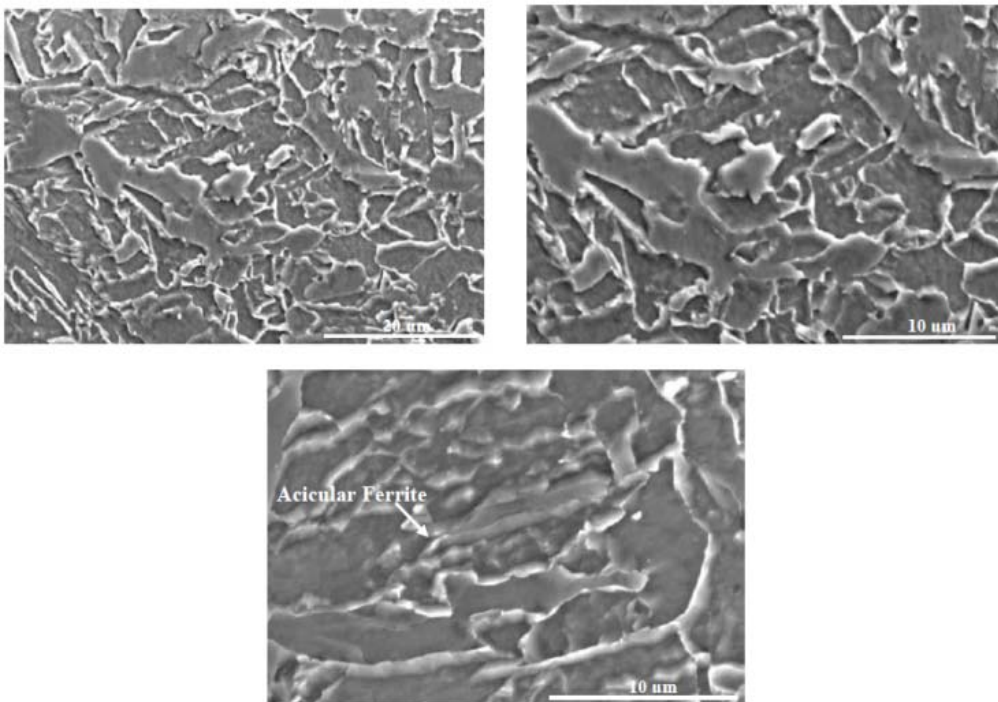

Fig. 16- SEM analysis characterization of Alloy A

Fig. 17 - TEM analysis characterization of Alloy A

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Alloy B, a standard API X80 (C-Mn-Si-Nb) alloy design, was characterized as approximately 90% polygonal ferrite and 10% coarse acicular ferrite. The acicular ferrite was only 10% by volume fraction and coarse, which was somewhat different than what was originally expected. Optical microscopy, SEM and TEM analysis can be seen in **Figures 18, 19 and 20** respectively.

Polygonal ferrite and coarse acicular ferrite
Fig. 18 - Optical microscopy characterization of Alloy B

Coarse Acicular Ferrite is more apparent in TEM micrographs

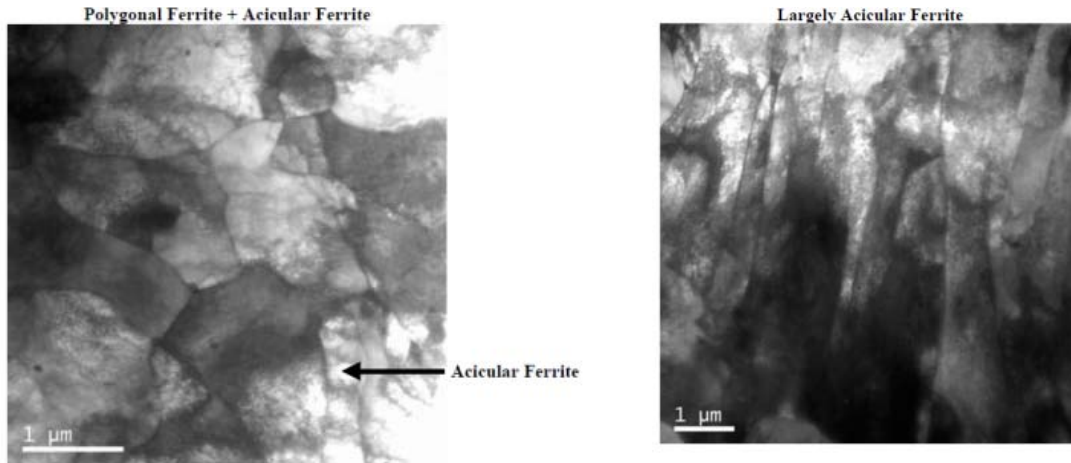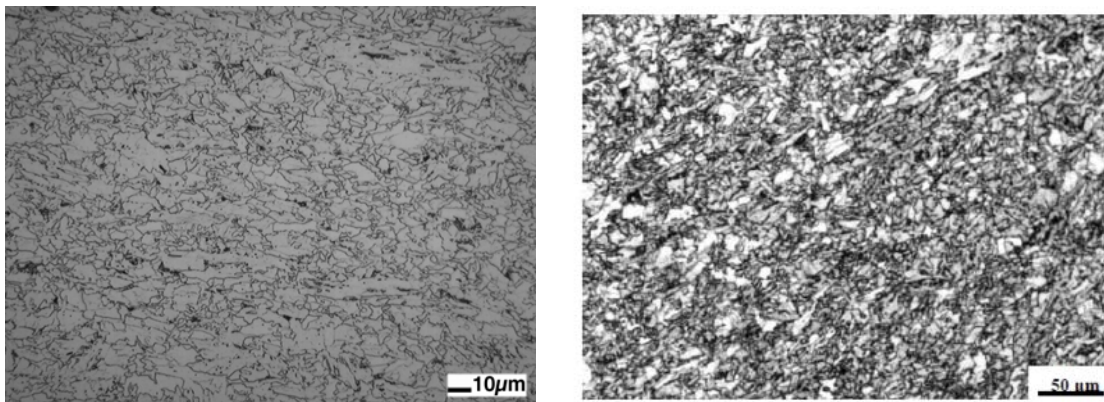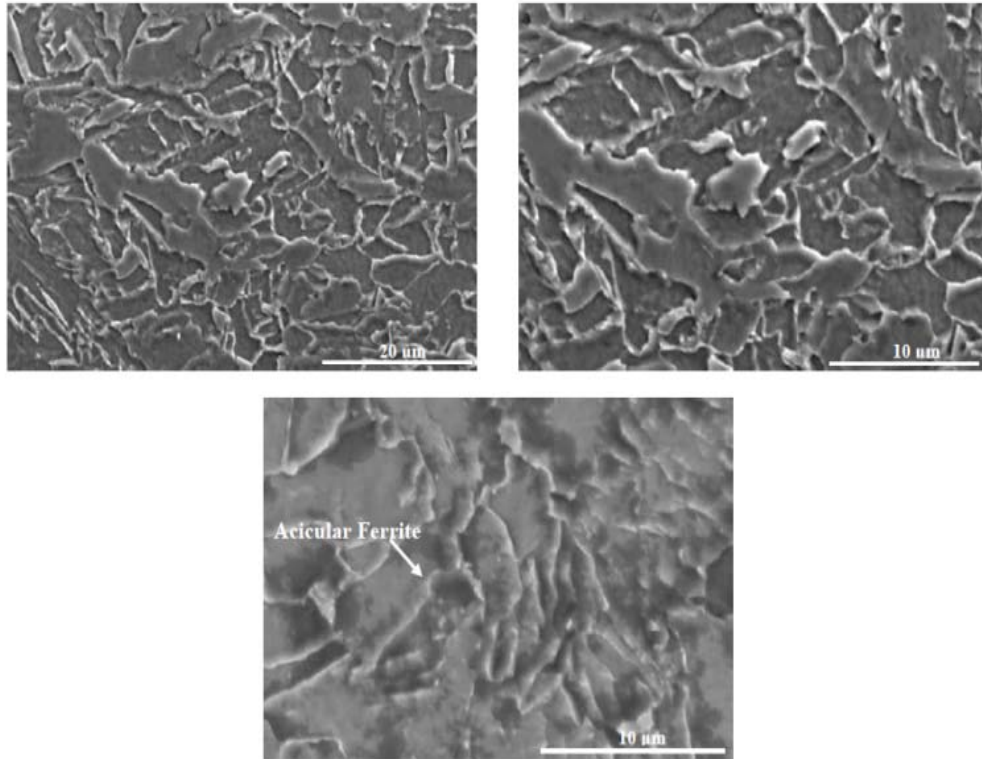**Fig. 19 - SEM analysis characterization of Alloy B**

Fig. 20 - TEM analysis characterization of Alloy B

Alloy C, a standard API X80 alloy design ((C-Mn-Si-Nb) with more solute elements than Alloy B) was characterized as approximately 90% polygonal ferrite and 10% predominately coarse acicular ferrite, but with very small amount of upper bainite. The acicular ferrite with a very small amount of upper bainite was only 10% by volume fraction and coarse, which again was somewhat different than what was originally expected. Optical microscopy, SEM and TEM analysis can be seen in **Figures 21, 22 and 23,** respectively. The upper bainite has been delineated in optical light, SEM and TEM microscopy. The dark appearance of upper bainite is characterized in the light microscope. Due to the low carbon level of 0.04%C in Alloy C, the upper bainite is lathe ferrite with very limited carbon precipitation between the laths.

Dark Islands Identified as Upper Bainite
Fig. 21 - Optical microscopy characterization of Alloy C

Coarse Acicular Ferrite is more apparent in TEM micrographs

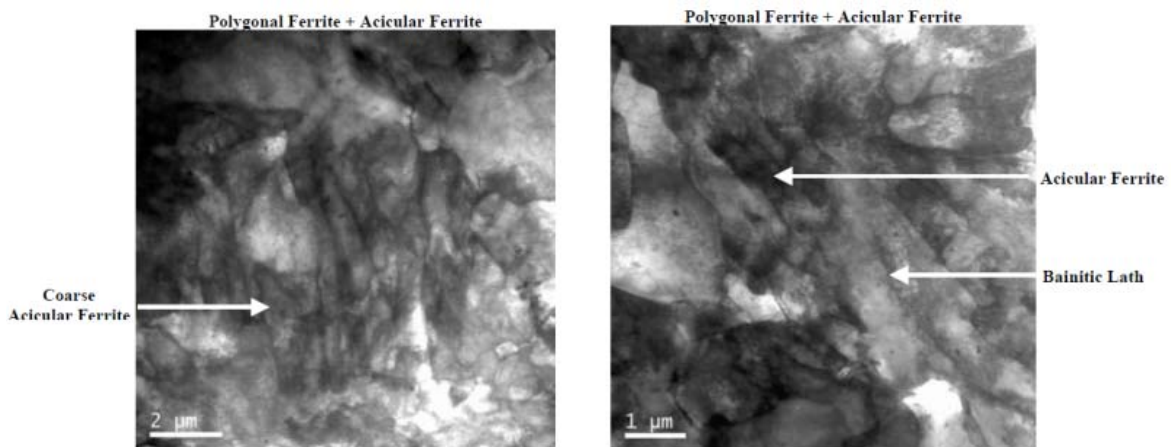**Fig. 22 - SEM analysis characterization of Alloy C**

Fig. 23 - TEM analysis characterization of Alloy C

Alloy D, an API X60 HIC design for low pH sour service natural gas applications (low C-Mn-Si-Nb), was characterized as 100% polygonal ferrite, which was somewhat different than originally expected. Optical microscopy, SEM and TEM analysis can be seen in **Figures 24, 25 and 26,** respectively.
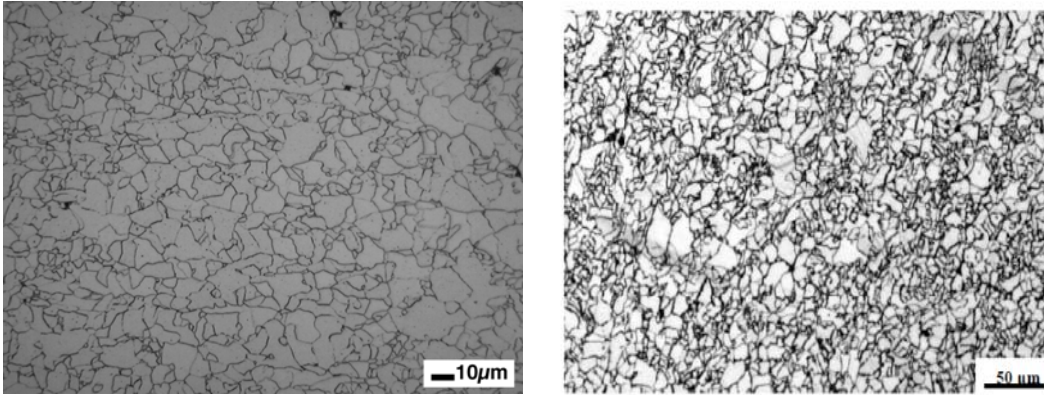
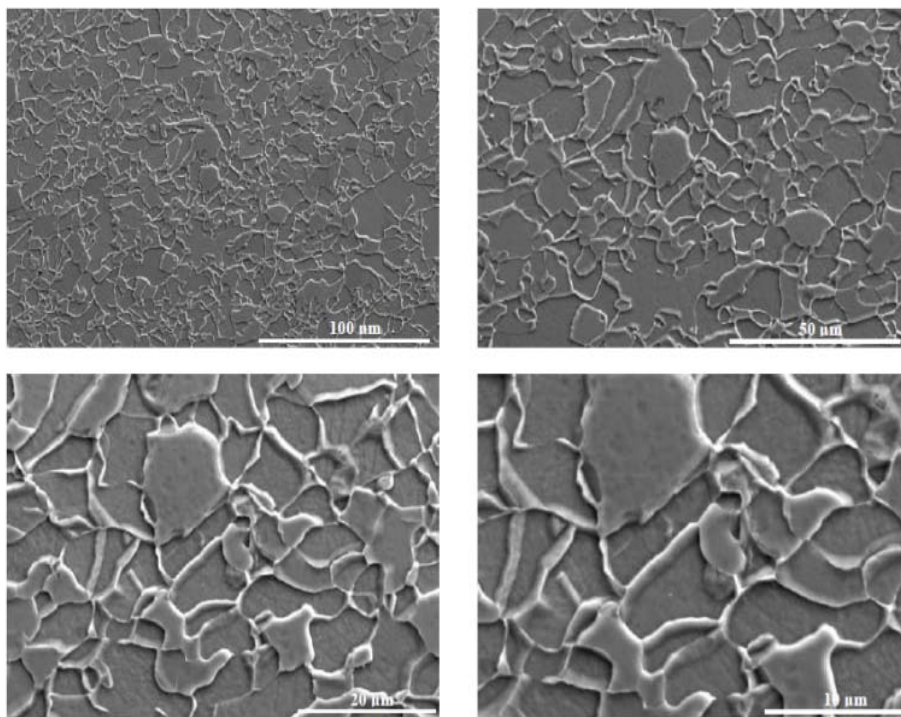**Fig. 24 - Optical microscopy characterization of Alloy D**

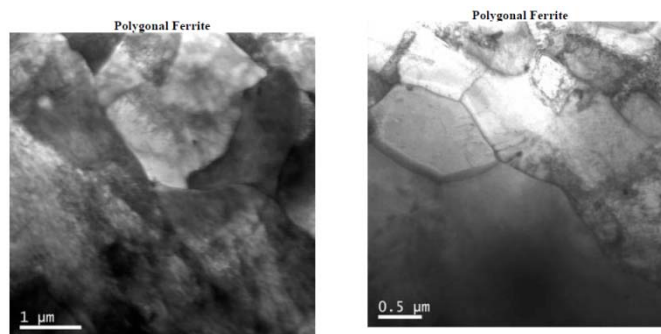**Fig. 25 - SEM analysis characterization of Alloy D**

Fig. 26 - TEM analysis characterization of Alloy D

Even though non-pipeline steel Alloy's E and F were not slated for further evaluation in the project, microstructural characterization was completed on them for future reference.

Alloy E was a low C, high Mn, Ni, B and Nb microalloyed steel produced by Thermo-Mechanical Control Processing (TMCP) rolling followed by accelerated water cooling (ACC) generating a minimum of 100 ksi (690 MPa) yield strength intended for structural applications such as crane booms. The microstructure was characterized as 100% acicular ferrite. SEM and TEM analysis can be seen in **Figures 27** and **28**.

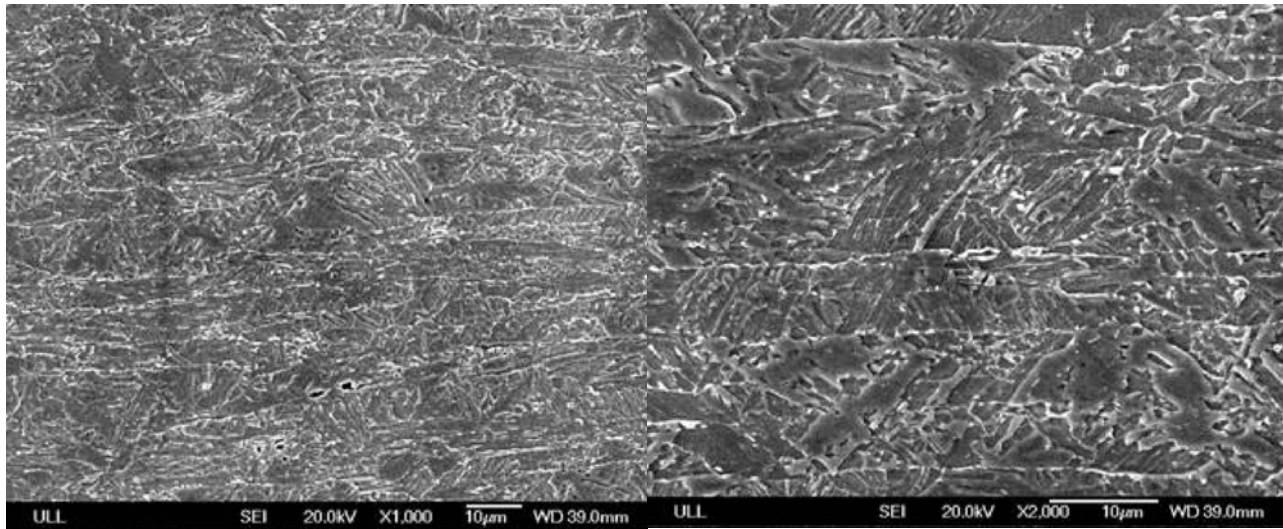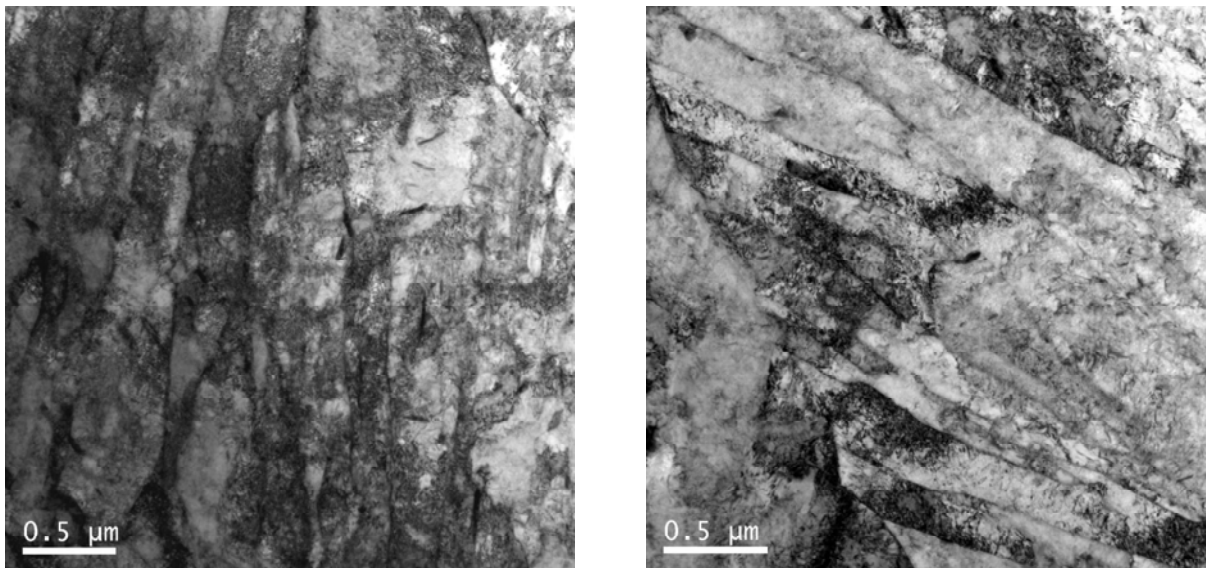**Fig. 27 – SEM analysis characterization of Alloy E**

Fig. 28 – TEM analysis characterization of Alloy E

Alloy F was a medium C, high Mn, Mo, Cr, B and Nb microalloyed steel produced by austenitizing (heat treatment) followed by water quenching and subsequent furnace tempering (Q&T) generating a minimum of 400 BHN hardness intended for abrasion resistant structural applications such as concrete trucks, dump

trucks, etc. The microstructure was characterized as 80% acicular ferrite plus 20% lath-type bainite. SEM and TEM analysis can be seen in **Figures 29** and **30**.
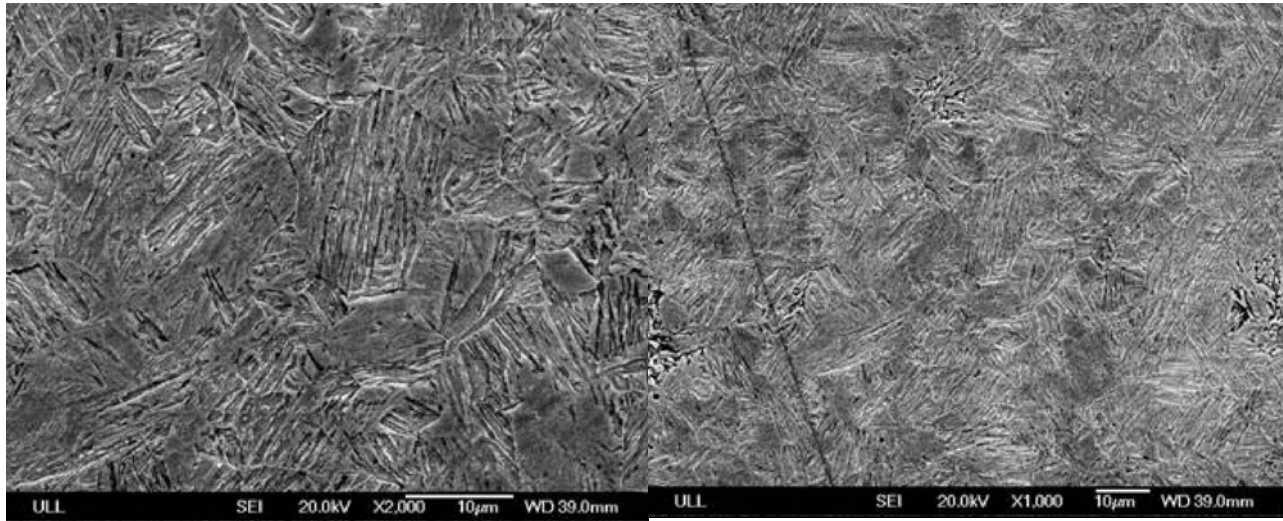
Fig. 29 – SEM analysis characterization of Alloy F
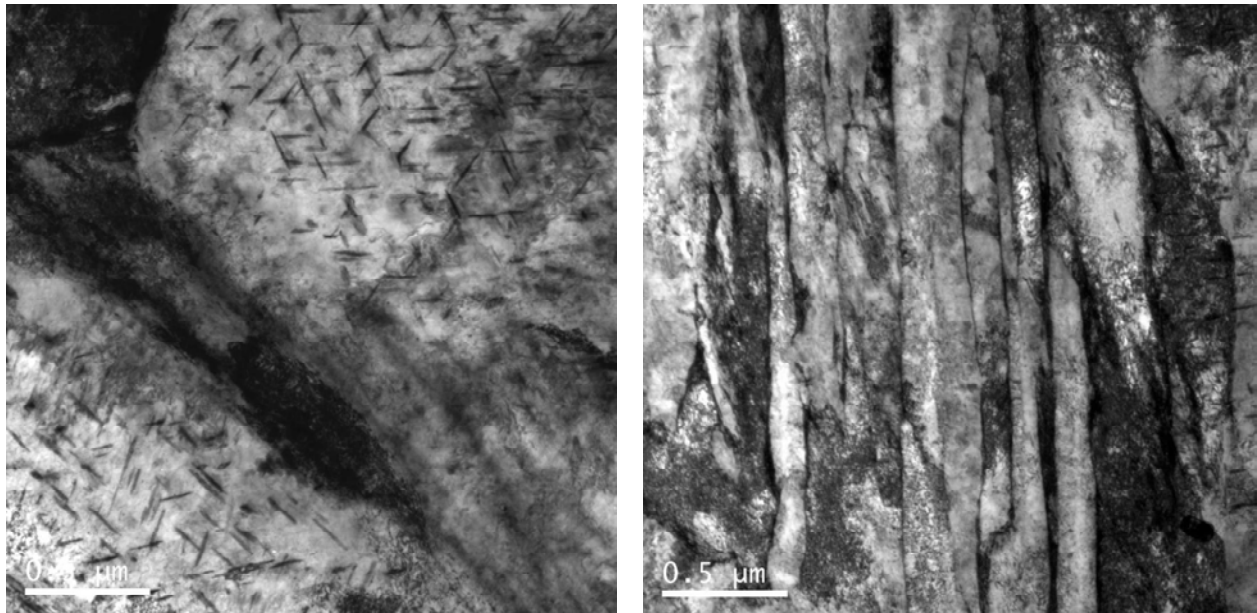
Fig. 30 – TEM analysis characterization of Alloy F

Tensile Test Results in Hydrogen

Tensile testing in the presence of helium and hydrogen gas was performed at Oak Ridge National Laboratory in Oak Ridge, TN. Helium was used and tested at all pressures as the baseline for comparison. Pressures of 5.5 MPa (800 psi), 11 MPa (1600 psi) and 20.7 MPa (3000 psi), representing potential operating pressures of a hydrogen gas transmission pipeline, were used. Two strain rates (10^{-4} and 10^{-5}) were explored. In all 48, tensile tests were performed in the presence of helium and hydrogen. Reduction in area (RA), a measure of the tensile ductility of metals, was reduced by testing in gaseous hydrogen.

Thus, it is used as a metric for the effects of gaseous hydrogen during tensile testing, as shown for the 5.5 MPa (800 psi) testing of Alloy A in **Figure 31**.

5.5 MPa (800 psi) He,
1x10^{-4}/sec, 78% RA with a standard "cup and cone" fracture feature and good "necking" showing good ductility.

5.5 MPa (800 psi) H$_2$,
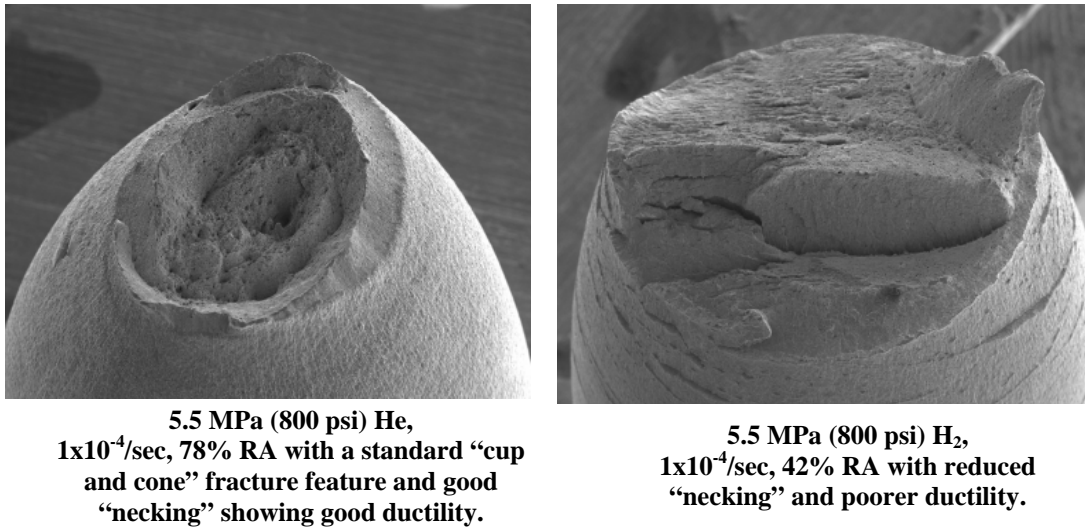1x10^{-4}/sec, 42% RA with reduced "necking" and poorer ductility.

Fig. 31 - Helium vs. hydrogen testing of alloy A at 5.5 MPa (800 psi) showing loss of ductility

The results of the testing are provided in **Figures 32 and 33** for the two strain rates, respectively. For both strain rates, the reduction in area in helium is close to 80% or greater, which is expected for these steels. At 5.5 MPa (800 psi) for both strain rates, the tensile ductility (RA) is significantly reduced for all alloys, although some alloys/microstructures perform slightly better. Beyond 5.5 MPa (800 psi), even though there is some variability in the data, especially at the 10^{-4} strain rate, a trend of no significant further reduction in tensile ductility. This demonstrates that volume fractions of phases affects the performance in gaseous hydrogen. This becomes more pronounced as the pressure is increased up to 20.7 MPa (3000 psi).
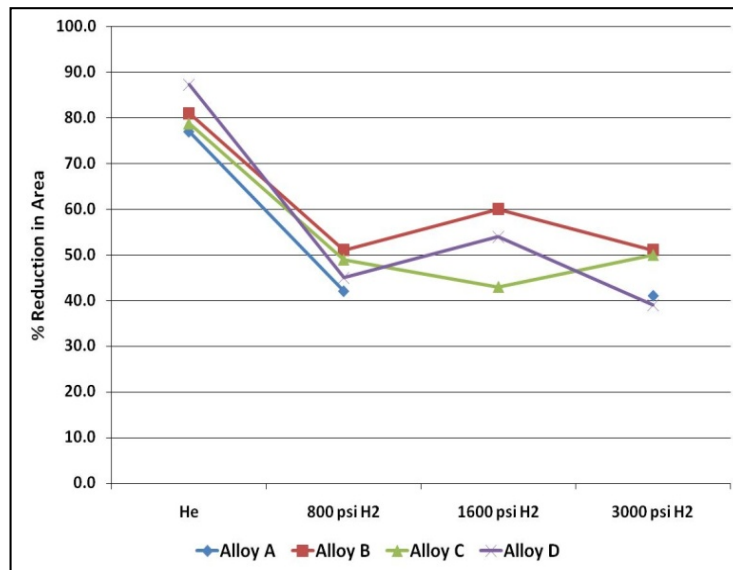

Fig. 32 - % Reduction in area comparison at strain rate of 10^{-4} for helium and hydrogen tensile testing at pressure
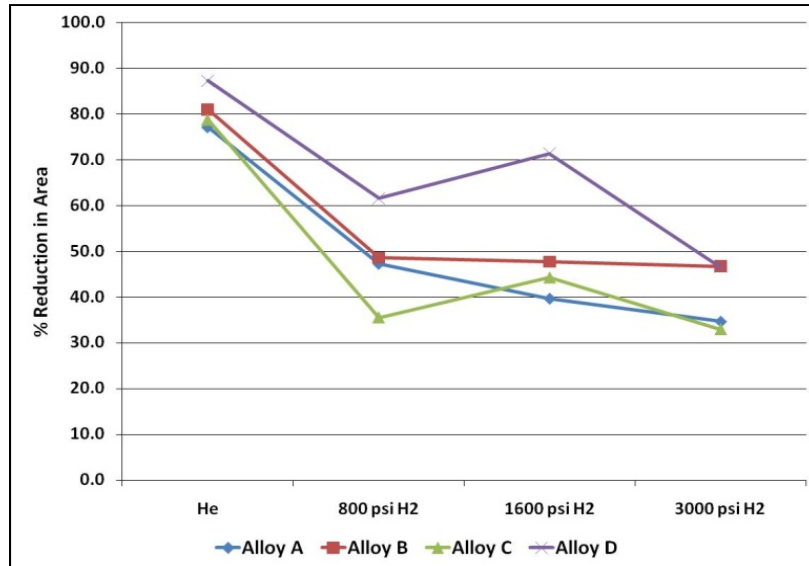
Fig. 33 - % Reduction in area comparison at strain rate of 10^{-5} for helium and hydrogen tensile testing at pressure

In this testing, the two microstructures that were devoid of any upper bainite, Alloys B and D, in general performed better at each strain rate with increasing hydrogen pressure. In fact, the tensile ductility of Alloy B is relatively insensitive to the hydrogen pressure and is approximately 50% for all three pressures.

The YS and TS were not altered in the presence of hydrogen. Only the fracture stress showed variability in hydrogen. This is illustrated for Alloy B in **Figure 34**.

Fig. 34 - Illustration of yield strength, ultimate strength and fracture stress performance for Alloy B

From the results of this tensile testing, Alloys B and D were chosen for further evaluation in fracture and fatigue testing.

Fracture and Fatigue Testing Results

Alloys B and D were selected for additional testing based on their tensile performance in gaseous hydrogen. Fracture and fatigue testing 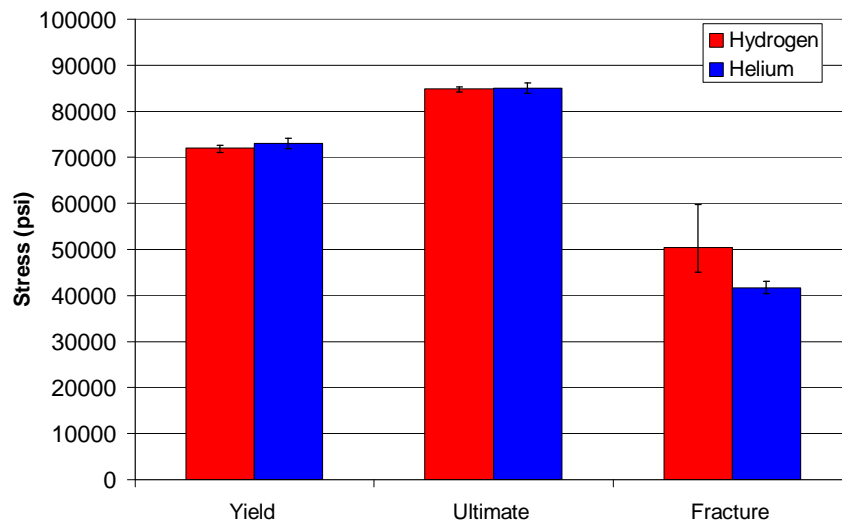was carried out at Sandia National Laboratory in Livermore, CA at gaseous hydrogen pressures of 5.5 MPa (800 psi) and 20.7 MPa (3000 psi). All fracture measurements were performed according to ASTM E1820-09. Stable crack extension was observed in all cases and the fracture toughness was determined by constructing J-R curves for each test. The details of the testing method and fracture measurements in gaseous hydrogen are given in paper "*Fracture and Fatigue of Commercial Grade API Pipeline Steels in Gaseous Hydrogen*"[11].

The measured fracture toughness in gaseous hydrogen is greater for Alloy B than Alloy D, as shown in **Figure 35**.

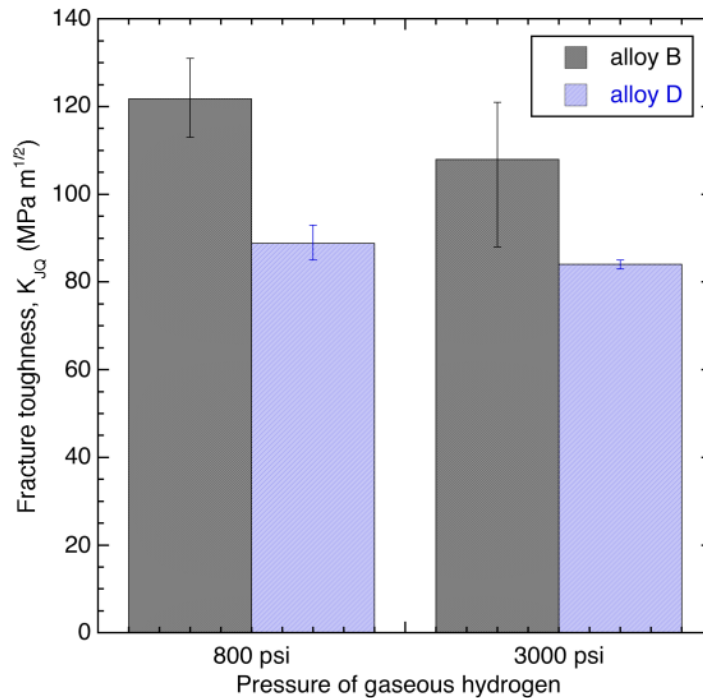**Fig. 35 - Fracture toughness measured in gaseous hydrogen. The error bars represent the minimum and maximum measured values (replicate specimens were measured for all conditions, except alloy B at pressure of 3000 psi, for which three measurements were made)**

These results do not follow the basic trend of decreasing fracture toughness for greater yield strength as Alloy B has higher strength than Alloy D, **Figure 36**.
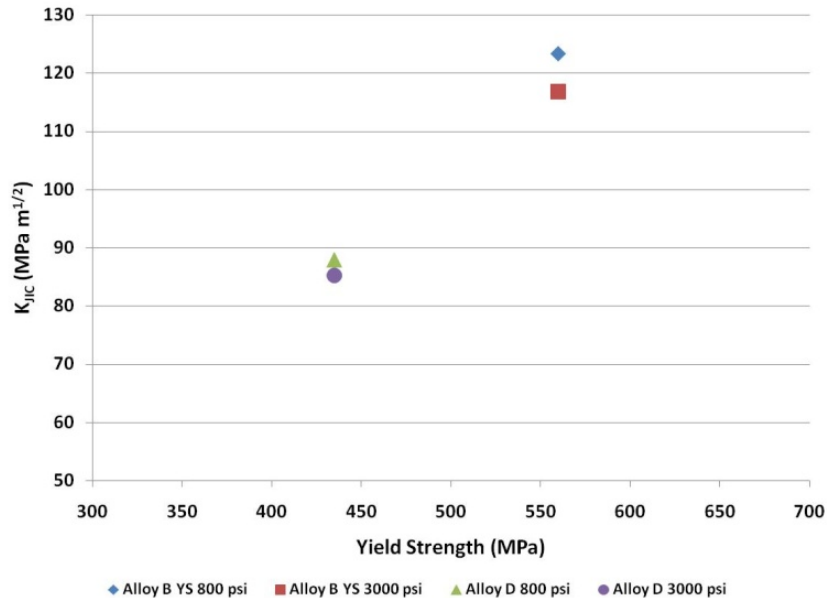
Fig. 36 - Strength vs. fracture toughness results for Alloys B and D

The strength difference between these alloys, however, is relatively small. Thus microstructural differences likely account for the difference of fracture resistance between these two alloys in gaseous hydrogen. In addition, the effect of pressure is relatively small: the fracture toughness decreases by 5-12% for an almost four-fold increase of hydrogen pressure.

Even though both microstructures have reasonable fracture toughness, the ferrite/10% coarse acicular ferrite microstructure of Alloy B performed better than that of 100% polygonal ferrite microstructure of Alloy D.

The fracture toughness of these alloys in air could not be measured with the given geometry (because the fracture toughness of the alloys is very large, which precluded crack growth in favor of global plastic deformation), which demonstrates that these alloys are strongly affected by exposure to gaseous hydrogen as observed in the tensile tests. Nevertheless, the critical stress intensity factor for crack advance (namely the fracture toughness) in gaseous hydrogen is unlikely to be exceeded for small cracks with modest ratio of length to crack depth. For example, consider a 10-inch diameter pipe with a wall thickness of 0.3 in. operating in gaseous hydrogen pressure of 10.3 MPa (1500 psi). The stress intensity factor associated with a through-wall crack (with length of twice the thickness) in the longitudinal direction will be less than 50 MPa m$^{1/2}$, which is significantly less than the fracture toughness that was measured in gaseous hydrogen.

Fatigue testing was also conducted at 5.5 MPa (800 psi) and 20.7 MPa 3000 psi) and a frequency of 1 Hz. In addition, tests were performed at two R-ratios, 0.5 and 0.1 (R is the ratio of the minimum to maximum load applied to the specimen). For a given set of test parameters, the fatigue crack growth rate (FCGR) in gaseous hydrogen is similar for both alloys, as shown in **Figure 37**. In general, the results of the fatigue testing show that the two alloys/microstructures perform approximately the same for values of R-ratio and pressure that were tested.
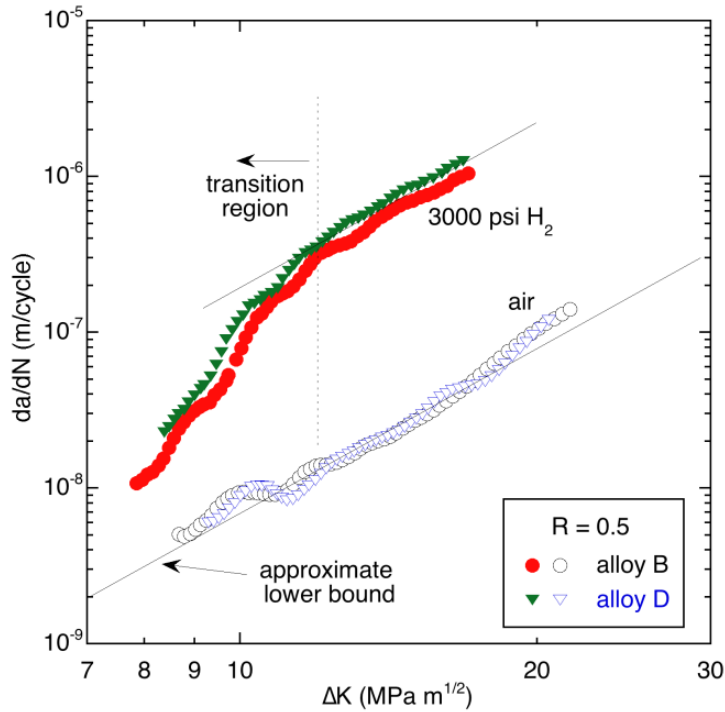
Figure 37: Fatigue crack growth of Alloy B and Alloy D in gaseous hydrogen at pressure of 3000 psi, compared to fatigue in air

At relatively high ΔK (> 12 MPa m$^{1/2}$), the FCGR in gaseous hydrogen is about 20 times greater than in air. At lower ΔK, however, the FCGR in air and in gaseous hydrogen begin to converge, **Figure 38**. Presumably at values of ΔK that are generally lower than measured in this study, the curves converge and the FCGR in gaseous hydrogen is the same as in air. However extrapolation to small values of ΔK must be done with caution and consideration for the bounding FCGR in air.
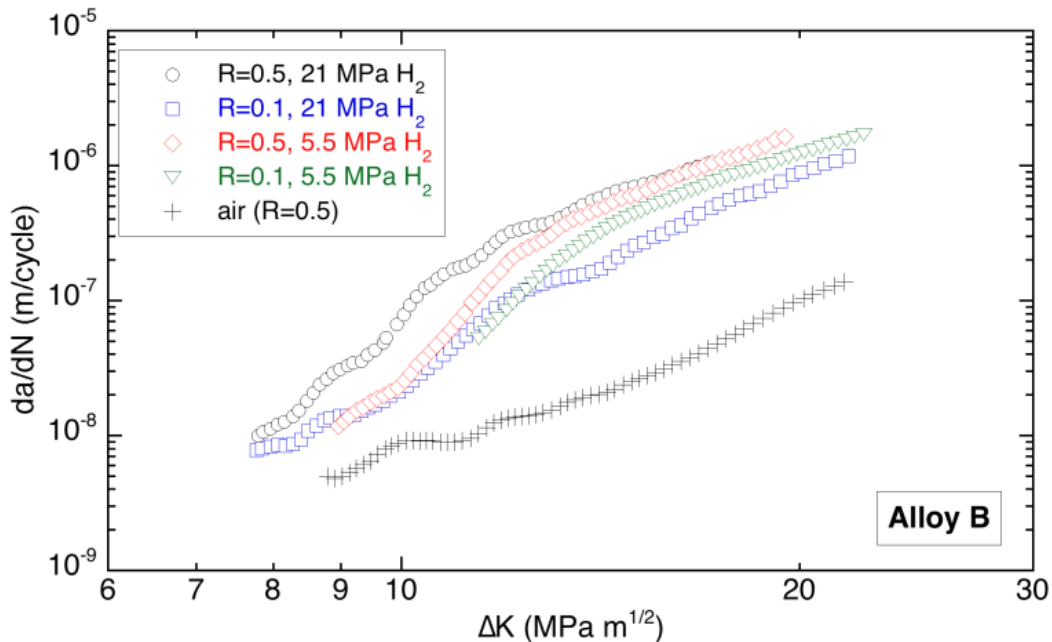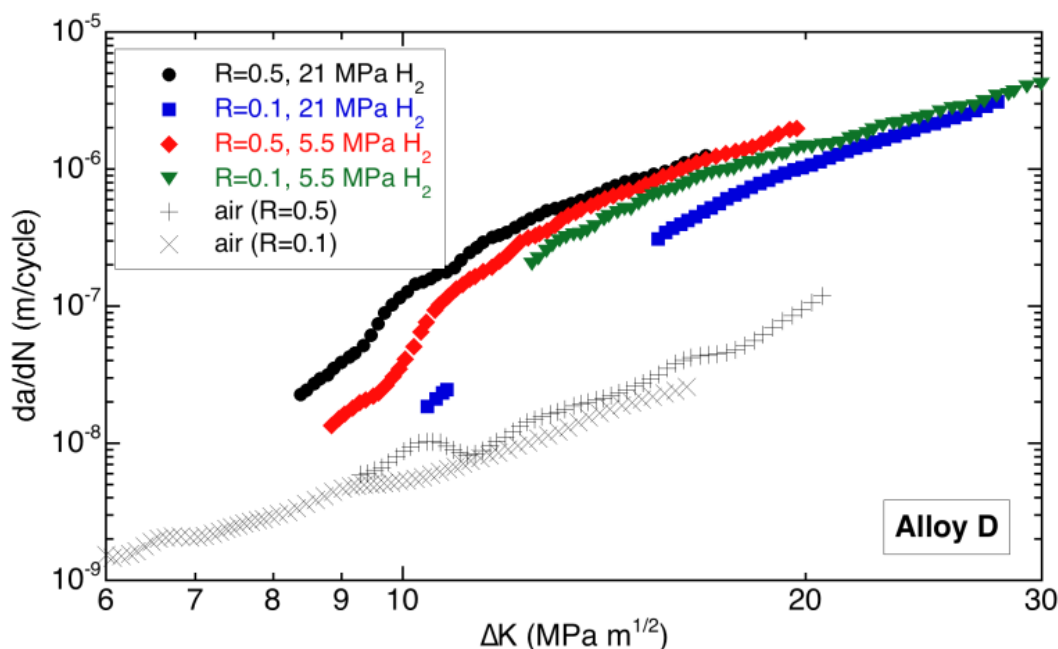
Fig. 38 - Measured fatigue crack growth rates for Alloy B and D

For example, extrapolating measured FCGRs to $\Delta K < 5$ MPa m$^{1/2}$ implies that the rate of crack growth is less in gaseous hydrogen than in air, which is unlikely. Near the FCGR threshold, however, there may be some differences between tests in gaseous hydrogen and in air as has been observed[12]. Testing at $\Delta K < 7$ MPa m$^{1/2}$ was not pursued in this study because of the length of the tests; a test at 1 Hz can require many days to complete (in constant load amplitude tests) when the crack growth rates are less than 10^{-8} m/cycle.

Figure 38 clearly shows a transition from high FCGRs in gaseous hydrogen at high ΔK to FCGRs that are closer to those measured in air at relatively low ΔK. The transition region depends on R-ratio and pressure. For R = 0.5, this transition region occurs in the range of ΔK between about 6 and 12 MPa m$^{1/2}$ independent of the pressure (at least within the pressure range of this study). For R = 0.1, the transition to lower FCGRs is shifted to greater values of ΔK. This is an effect of the greater absolute value of the stress intensity factor applied to specimen at higher values of R for the same value of ΔK (e.g., for $\Delta K = 15$ MPa m$^{1/2}$, $K_{max} = 30$ MPa m$^{1/2}$ for R = 0.5, and $K_{max} = 16.7$ MPa m$^{1/2}$ for R = 0.1). The higher stress associated with the higher stress intensity factor will facilitate the effects of hydrogen. The measured FCGRs, however, converge for all the tested conditions at high values of ΔK, suggesting that the effect of stress saturates prior to reaching the critical stress intensity factor for rapid fracture.

The effect of pressure (at least for the range explored in this study) appears to be modest for ΔK less than about 6 MPa m$^{1/2}$ (based on extrapolation) and ΔK greater than about 20 MPa m$^{1/2}$; i.e., the effect of pressure is nominally bounded by the FCGR in air at low ΔK and the limiting FCGR at large ΔK. In the transition region between the air bound and the high limit in gaseous hydrogen, FCGRs are generally lower at the lower pressure, particularly for R = 0.1. This is expected since the effects of hydrogen are enhanced as pressure is increased.

The FCGRs in the transition region are arguably the most important for systems that experience significant numbers of pressurization cycles. The high ΔK region is not of particular interest because FCGRs greater than about 10^{-6} m/cycle are sufficiently rapid that cracks can extend millimeters in

hundreds of cycles (and accelerating for a given pressure cycle). Crack-like defects in real pressurized structures (as often assumed in pipelines and pressure vessels) can induce significantly large stress intensity factors at the defects: K_{max} of 10 MPa m$^{1/2}$ is relevant for defects near the detection limit in structures operating at a large fraction of the nominal yield stress of the material. Therefore, understanding the transition between FCGRs that are similar to air and those that are 20 times greater is important and necessary.

Technical Accomplishment

The project successfully demonstrated that steel microstructures do a play a role in the mechanical performance of various pipeline steels when exposed to gaseous hydrogen in pressures in the range of 800 to 3000 psi.

Screening techniques such as NACE TM0284 and tensile testing in the presence of hydrogen can be used to determine a given steels microstructure overall performance in the presences of gaseous hydrogen.

Fracture toughness is a critical path to microstructure design for gaseous hydrogen service up to 3000 psi pressure. Fatigue performance plays a lesser role in this regard at the pressure ranges studied.

Pipelines with a minimum designed yield strength up to API X70 can potentially be used in hydrogen service as long as the appropriate microstructure of polygonal ferrite/acicular ferrite can be developed through alloy and process design.

Technology Transfers

During the entire project as data was being generated along with the additional information generated in the non-DOE funded "Phase 2" program, the testing parameters and results have been shared with various organizations/team members. Presentations have been made at each US DOE Annual Peer Review Meeting, at each DOE Pipeline Working Group meeting, paper/presentations at ASME PVP 2009, 2010, 2011 and the upcoming 2013 conferences, ASME International Pipeline Conferences in 2010 and 2012, 2008 and 2012 International Hydrogen Conference and with the ASME B31.12 Piping and Pipelines codes and standards committee. Project partner DGS Metallurgical Solutions, Inc. is a member of the ASME B31.12 codes and standards committee and is working with the committee to make guidance language modifications to the existing B31.12 code based on the results of the work from the original DOE funded project and additional "Phase 2" work. The ASME B31.12 committee has representation from three large industrial hydrogen producers which have access to the data generated by the initial program and the "Phase 2" program demonstrating the importance of proper microstructure selection in optimizing the design of hydrogen piping and pipeline systems.

Publications and Presentations

Publications

1. Stalheim, D., Govindarajan, M., *"The Role of Continuous Cooling Transformation Diagrams for High Strength Oil and Gas Transmission Pipeline Steels"* - Proceedings and Presentation at the 6th ASME International Pipeline Conference, Calgary, Canada, September 2006.

2. Hayden, L., Stalheim, D., *"Metallurgical Considerations for Commercial Steels used for Hydrogen Service"* - Proceedings and Presentation at Hydrogen08 Conference, Jackson Hole, WY USA September 2008.
3. Govindarajan, M., et.al., *"Effect of Microstructure on Hydrogen Embrittlement Characteristics of Selected Pipeline Steels"* - Presented at Hydrogen08 Conference, Jackson Hole, WY USA September 2008.
4. Hayden, L., Stalheim, D., *"ASME B31.12 Hydrogen Piping and Pipeline Code Design Rules and their Interaction with Pipeline Materials Concerns, Issues and Research"* - Proceedings of PVP2009, 2009 ASME Pressure Vessels and Piping Division Conference, Prague, Czech Republic, July 2009.
5. San Marchi, C., et.al., *"Fracture and Fatigue of Commercial Grade API Pipeline Steels in Gaseous Hydrogen"*, Presentation and Proceedings of the ASME 2010 Pressure Vessels & Piping Division / K-PVP Conference, Bellevue, WA USA, July 2010.
6. Stalheim, D., et.al., *"Microstructure and Mechanical Property Performance of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen"*, Proceedings and Presentation at the 8th ASME International Pipeline Conference, Calgary, Canada, September 2010.
7. San Marchi, C., et.al., *"Fracture Toughness and Fatigue Crack Growth of X80 Pipeline Steel in Gaseous Hydrogen"*, Proceedings of the ASME 2011 Pressure Vessels & Piping Division / K-PVP Conference, Baltimore, MD, USA, July 2011.
8. Stalheim, D., et.al., *"Continued Microstructure and Mechanical Property Performance of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen"*, Proceedings and Presentation at the 9th ASME International Pipeline Conference, Calgary, Canada, September 2012.
9. Stalheim, D., et.al., *"Microstructure and Mechanical Property Performance Evaluation of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen"*, 2012 International Hydrogen Conference– Hydrogen – Materials Interactions, Jackson Hole, Wyoming, USA, September 2012.

Presentations

1. *"Materials Solutions for Hydrogen Delivery in Pipelines"* – Summary of US Department of Energy Funded Research and Development Effort of Hydrogen Fuel Cells and Infrastructure Technologies Program, US Department of Energy Workshop, Augusta, GA USA, August 2005.
2. *"On the Development of Fracture Criteria for Hydrogen Embrittlement of Pipeline Steels"* – Discussion on Fracture Mechanics in Hydrogen Embrittlement of API Pipeline Steel. A collaboration with the University of Illinois, Sandia National Laboratories, and Oak Ridge National Laboratories. Presented at ASTM TF G.01.06.08 Hydrogen Gas Embrittlement Workshop, Dallas, Texas USA, November 2005.
3. *"Materials Solutions for Hydrogen Delivery in Pipelines"* – Summary of US Department of Energy Funded Research and Development Effort of Hydrogen Fuel Cells and Infrastructure Technologies Program, Arlington VA USA, May 2006.
4. *"Material Challenges in the Use of High Strength Steel Pipelines for High Pressure Hydrogen Gas Transmission"* – 2nd Hydrogen Panel Forum "Hydrogen Pipeline Transmission: Updates and Opportunities", 6th ASME International Pipeline Conference, Calgary, Canada, September 2006.
5. *"Materials Solutions for Hydrogen Delivery in Pipelines"* – Department of Energy Pipeline Working Group for Hydrogen Delivery, Sandia National Laboratory, Livermore, CA USA, February 2008.
6. *"Materials Solutions for Hydrogen Delivery in Pipelines-Peer Review"* – Department of Energy Peer Review Meeting for Hydrogen Delivery, Arlington, VA USA, June 2008.

7. *"Materials Solutions for Hydrogen Delivery in Pipelines - Update"* – Department of Energy Pipeline Working Group for Hydrogen Delivery, Jackson Hole WY USA, September 2008.
8. *"Alloy/Processing/Microstructure Designs for High Strength Transmission Pipeline Steels"* - Department of Energy Pipeline Working Group for Hydrogen Delivery, Jackson Hole WY USA, September 2008.
9. *"Materials Solutions for Hydrogen Delivery in Pipelines-Peer Review"* – Department of Energy Peer Review Meeting for Hydrogen Delivery, Arlington, VA USA, May 2009.
10. *"Materials Solutions for Hydrogen Delivery in Pipelines - Update"* – Department of Energy Pipeline Working Group for Hydrogen Delivery, NIST Boulder, CO USA, August 2009.
11. *"Materials Solutions for Hydrogen Delivery in Pipelines-Peer Review"* – Department of Energy Peer Review Meeting for Hydrogen Delivery, Washington, DC USA, June 2010.
12. *"Materials Solutions for Hydrogen Delivery in Pipelines-Peer Review"* – Department of Energy Peer Review Meeting for Hydrogen Delivery, Arlington, VA USA, May 2011.

Summary, Conclusions and Recommendations

This originally funded DOE work coupled with the additional Phase 2 work has significantly increased the understanding of the role of steel alloy designs, microstructures and mechanical property performance when exposed to gaseous hydrogen in the pressure ranges of 800 – 3000 psi. Even though there is mechanical property degradation with initial exposure to hydrogen for all steels evaluated, mechanical property performance of certain microstructures can become stable with increasing hydrogen pressure. Mechanical property performance of certain microstructures may be more than adequate to perform safely for hydrogen gas service applications. This strongly implies that pipeline steels that exist in some of the current North American transmission pipeline infrastructure may be suitable for gaseous hydrogen transportation. It also strongly suggests that current pipeline steel technology can be used to develop microstructures that have suitable mechanical properties in the presence of gaseous hydrogen in pressures up to 3000 psi.

From this original DOE funded work the following conclusions can be made:

1. Pipeline steel microstructures evaluated in the project all experienced an initial degradation in mechanical properties with initial exposure to hydrogen gas under pressure (800 psi) as measured by reduction in area tensile testing.
2. However, once the initial degradation was reached, microstructures behaved differently with continued increasing hydrogen pressure up to 3000 psi.
3. Microstructures of polygonal ferrite and/or acicular ferrite with no presence of upper bainite or pearlite performed the best in hydrogen pressures up to 3000 psi as measured by reduction in area tensile testing.
4. Absolute yield and ultimate strength were not affected by exposure to hydrogen; only the stress to final fracture was affected by hydrogen.
5. Fracture toughness varied by microstructure with slight decreases in toughness with increasing hydrogen pressure for each of the two microstructures tested.
6. Fatigue testing between the two microstructures with two different frequencies and pressures showed no significant difference when exposed to hydrogen.
7. Since fatigue was not significant between the two microstructures then microstructure design to optimize fracture toughness can be considered. A polygonal ferrite/acicular ferrite microstructure generated the highest fracture toughness values up to 3000 psi of the two microstructures evaluated.

8. Increasing yield strength did not affect the fracture toughness performance in hydrogen up to 3000 psi as has been reported previously by others.
9. Even though the polygonal ferrite/acicular ferrite microstructure performed the best in this evaluation, this does not necessarily mean that some of the other microstructures are not suitable for hydrogen service. Suitability will have to be determined by the requirements of the piping/pipeline system transporting the hydrogen.

Based on the project work, the following recommendations can be made:

1. Correlations need to be developed between the fracture toughness/fatigue test results with those of a more traditional steel testing technique such as the V-notch Charpy toughness testing. The standard steel testing protocol then can be used in developing specifications.
2. Additional steel microstructures have been evaluated for fracture toughness since this original project, however, as illustrated in **Figure 9** there are still additional alloys/microstructures and probably a few more added to the matrix (X70 induction bend pipe as an example) that should be evaluated.
3. Fatigue testing needs to be completed as illustrated in the **Figure 9** matrix.
4. Various seam and girth welds need to be evaluated at 800 and 3000 psi. This includes submerged arc welded material along with other field welding techniques and consumable combinations.
5. Based on this work along with the additional work done in Phase 2, a clearer picture is developing of what an optimum metallurgical/alloy/microstructure hydrogen transmission pipeline may look like. A small (30-35 pipe lengths of a standard 40 feet length) rectangular demonstration pipeline should be built complete with a compressor station and monitoring equipment based on current knowledge and understanding. This line could be built and monitored at a national laboratory site such as Sandia National Laboratory – Livermore.

Acknowledgements

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