DOE Hydrogen Program

Materials Solutions for Hydrogen Delivery in Pipelines

Secat, Inc.

Presenter: Doug Stalheim,

DGS Metallurgical Solutions, Inc.

May 10, 2011

2011 U.S. DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting

Arlington, VA

Project ID – PD047

Overview

Timeline

- Project start date: 03/2005
- Project end date: 09/2011
- Percent complete: 95%

Budget

- Total project funding
  - $780K (DOE share)
  - $1,230K (contractor share)

Barriers and Targets

Barriers addressed

High capital cost and Hydrogen Embrittlement of Pipelines

Technical Targets (2017):

– Capital cost ($490K/Mile Transmission)

– Cost of delivery of hydrogen <$1.00/gge

– High Reliability of operation with metrics to be determined

Partners

SECAT CONSORTIUM

- **ASME Standards and Technologies**
- **Chemical Composite Coatings Intl**
- **Columbia Gas of Kentucky**
- **EVRAZ - Oregon Steel Mills**
- **Schott North America**
- **DGS Metallurgical Solutions, Inc.**
- **Hatch Moss MacDonald**
- **Oak Ridge National Laboratory**
- **University of Illinois**
- **Reference Metals Company**

Objective and Deliverables

Objective:

- Develop materials technologies to minimize embrittlement of steels used for high-pressure transport of hydrogen

Deliverables:

- **Most Important** - Identify steel compositions and processes suitable for construction of a new pipeline infrastructure or potential use of the existing steel pipeline infrastructure
- Develop barrier coatings for minimizing hydrogen permeation in pipelines and associated processes – **ON HOLD per DOE**
- Understand the economics of implementing new technologies

Objective Relevance

- **Known**
  - Variability of microstructure within a grade i.e. not all X52, X70, etc. is created equal
  - Disassociation of H_2 to H required
  - Disassociation causes – Corrosion, Partial Pressures
  - Surface oxide layers can inhibit diffusion of hydrogen into the steel
  - H migrates/collects in area of high residual stress (50% of residual stress due to microstructure mismatch, inclusions, thermal, mechanical)
- **Unknown**
  - H_2 embrittlement of steels/welds in high pressure dry gaseous H_2
  - Effect on steel metallurgical microstructures in high pressure dry gaseous H_2
  - Effectiveness of no-metallic coatings in minimizing H_2 issues
  - Economics of technical solutions not qualified
  - Is common X70 microstructure suitable in high pressure dry gaseous H_2 (Volume fraction? Banding? Moisture/corrosion?)
  - Suitability of alternative microstructures in high pressure dry gaseous H_2 (Volume fraction? Banding? Moisture/corrosion?)

Relevant Key Technical Barriers

- Hydrogen embrittlement of steels and welds exposed to high pressure dry gaseous H_2 is **not well understood**

- Effect of steel metallurgical microstructures on hydrogen embrittlement in a high pressure dry gaseous H_2 environment are **not known**

- Effectiveness of metallic and non-metallic coatings on minimizing H_2 embrittlement at high pressures has **not been studied**

- Economics of technological solutions to remediate the effect of hydrogen embrittlement has **not been quantified**

Milestones or Go/No-Go Decisions

Month/Year	Milestones or Go/No-Go Decisions
August 08	**Milestone:** Completed initial round of tensile testing in high pressure (800, 1600, 3000 psi) gaseous hydrogen of 4 down selected commercially available transmission pipeline steels.
September 08	**Go/No-Go Decision:** Using the scientific community recognized method for evaluation of hydrogen effect on tensile testing of reduction in area along with previous NACE testing for hydrogen cracking resistance and microstructural analysis, two of the best performing of the four down selected pipeline steels further evaluated with fracture toughness and fatigue testing in high pressure gaseous hydrogen.
May 09	**Milestone:** Complete final smaller validation round of tensile testing in high pressure gaseous hydrogen of four down selected commercially available transmission pipeline steels.
December 09	**Milestone:** Completed fracture toughness and fatigue testing in high pressure gaseous hydrogen of two selected commercially available pipeline steels based on Sept. 08 Go/No-Go Decision.
December 10	**Milestone:** Finish fracture and fatigue testing of additionally commercially available pipeline steels/microstructures.
September 11	**Milestone:** Summarize results and data into final report related to Task 1.

Major Tasks

Task 1: Evaluate hydrogen embrittlement characteristics of existing commercial pipeline base steels/microstructures and welds under high-pressure hydrogen gas

Task 2: Evaluate hydrogen embrittlement characteristics of existing commercial alternative alloy/microstructure steels under high-pressure hydrogen gas

Task 3: Develop Alternate Alloys/microstructure and welding consumables and Evaluate Hydrogen Embrittlement

Task 4: Financial Analysis and Incorporation into Codes and Standards

Note – Tasks related to coatings have been placed on hold and are not represented here. Focus of the project has shifted predominately to Tasks 1 and 2 and Task 4 incorporation of relevant information into Codes and Standards.

Progress To Date

a) **Four (4) commercial pipeline steels have been down-selected, X70, X70/X80, X70/X80, X52/X60 HIC**

- Majority of the baseline pipeline steel microstructure and mechanical property data have been characterized
- Commercial X70 pipeline welds available
- Two (2) traditional screening tests have been explored
- *In-situ* ABI test has been developed
- Processing techniques developed for glassy coatings
- Down-selected composition has been coated for properties and microstructural analyses
- *In-situ* tensile testing of all 4 alloys at ORNL complete
  - Two strain rates - $1x10^{-4}$, $1X10^{-5}$
  - Hydrogen vs. helium
  - 3 pressures – 800 psi, 1600 psi, 3000 psi
  - Total initial tests = 48, additional validation testing = 10, additional statistical testing of alloy A and B

Progress To Date

a) **Continued**

- Completed detailed microstructural characterization for the 4 selected pipeline steels.
- Completed fracture and fatigue testing completed of 2 selected pipeline steels at 800 and 3000 psi H_2 pressure at Sandia National Laboratory.

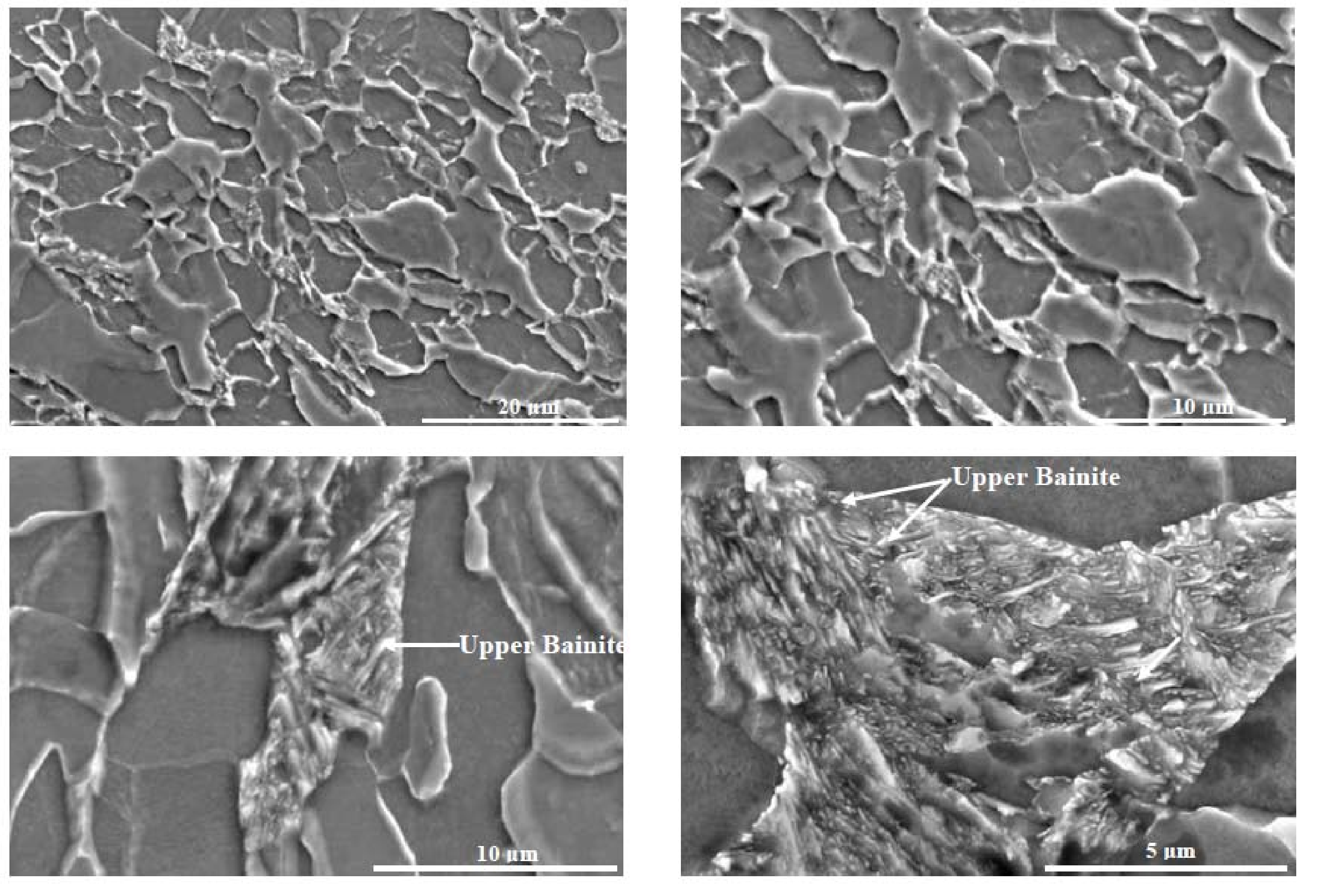
b) **Two (2) commercial abrasion resistant/structural steels have been down-selected**

- Low C abrasion resistant microstructural characterization complete – 100% Fine Acicular Ferrite
- Medium carbon-high alloy structural steel microstructural characterization complete – 80% acicular ferrite, 20% lath type bainite

Approach – Details of Microstructural Characterization of Steels Tested

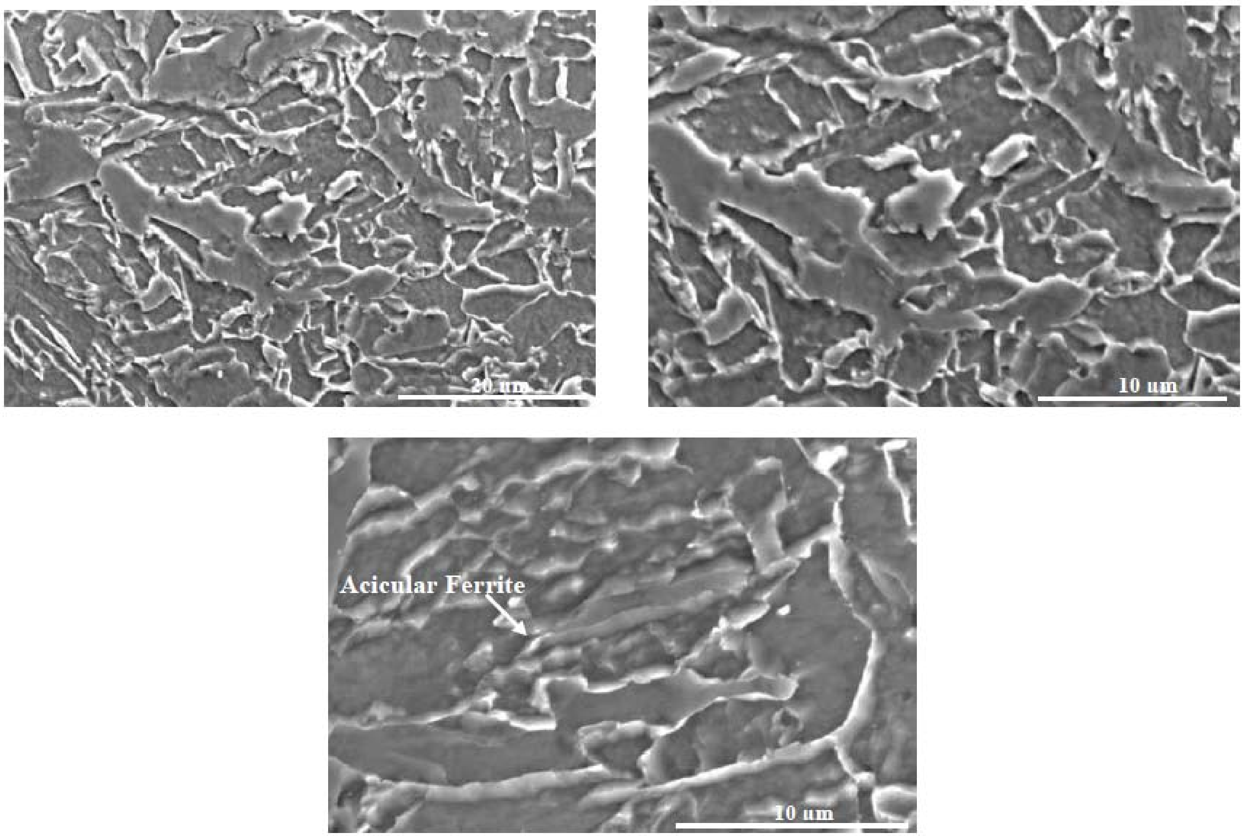
Alloy A (X70) – Polygonal Ferrite/Upper Bainite (Upper Bainite ~ 8%)

SEM Analysis



Approach – Details of Microstructural Characterization of Steels Tested

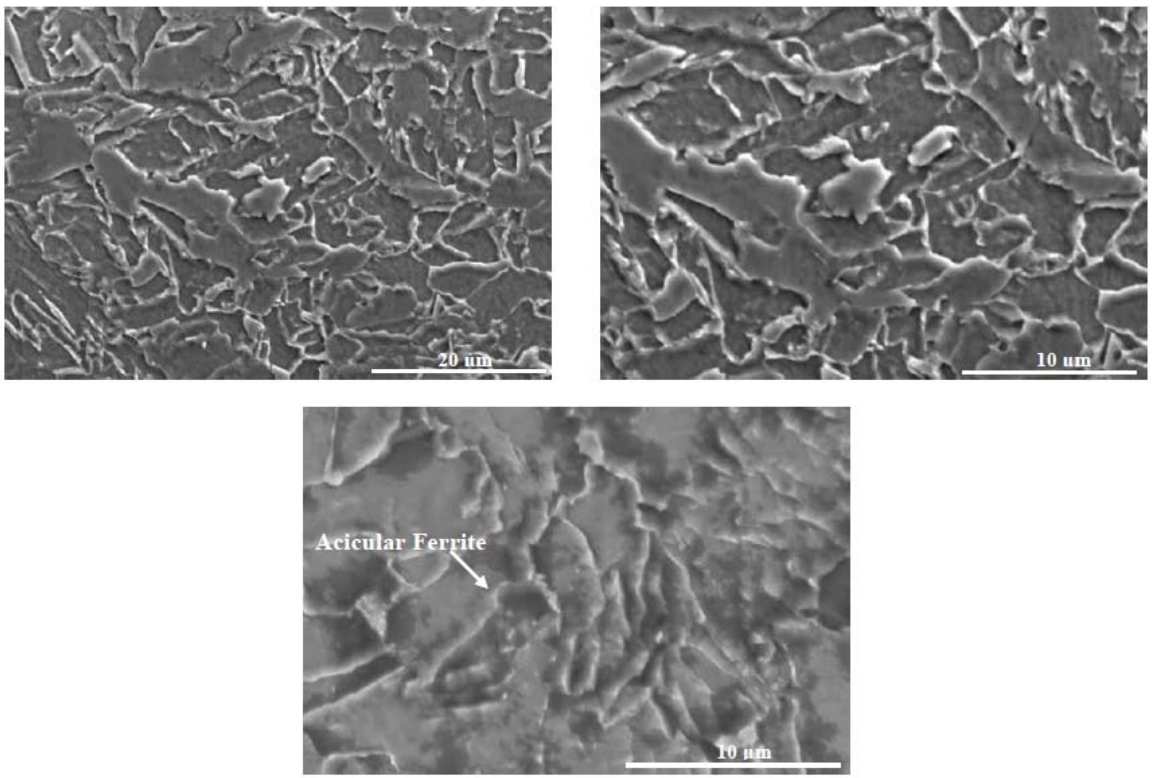
Alloy B (X70/X80) – Polygonal Ferrite/Coarse Acicular Ferrite (type of Bainite) ~ 10%, SEM Analysis



Coarse Acicular Ferrite is more apparent in TEM micrographs

Approach – Details of Microstructural Characterization of Steels Tested

Alloy C (X70/X80) – Polygonal Ferrite/Coarse Acicular Ferrite (type of Bainite), plus Upper Bainite ~ 10%, SEM Analysis

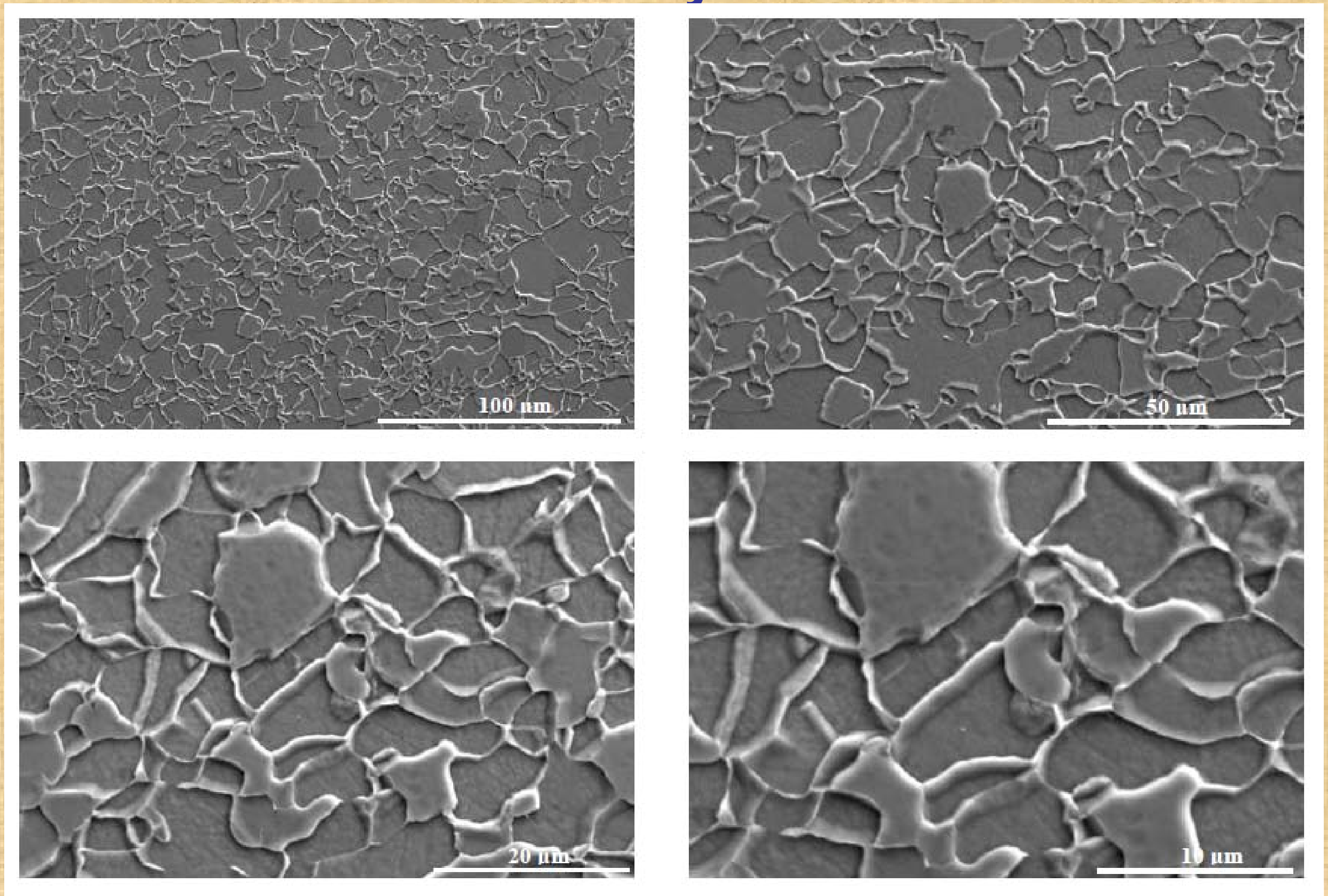


Coarse Acicular Ferrite is more apparent in TEM micrographs

Approach – Details of Microstructural Characterization of Steels Tested

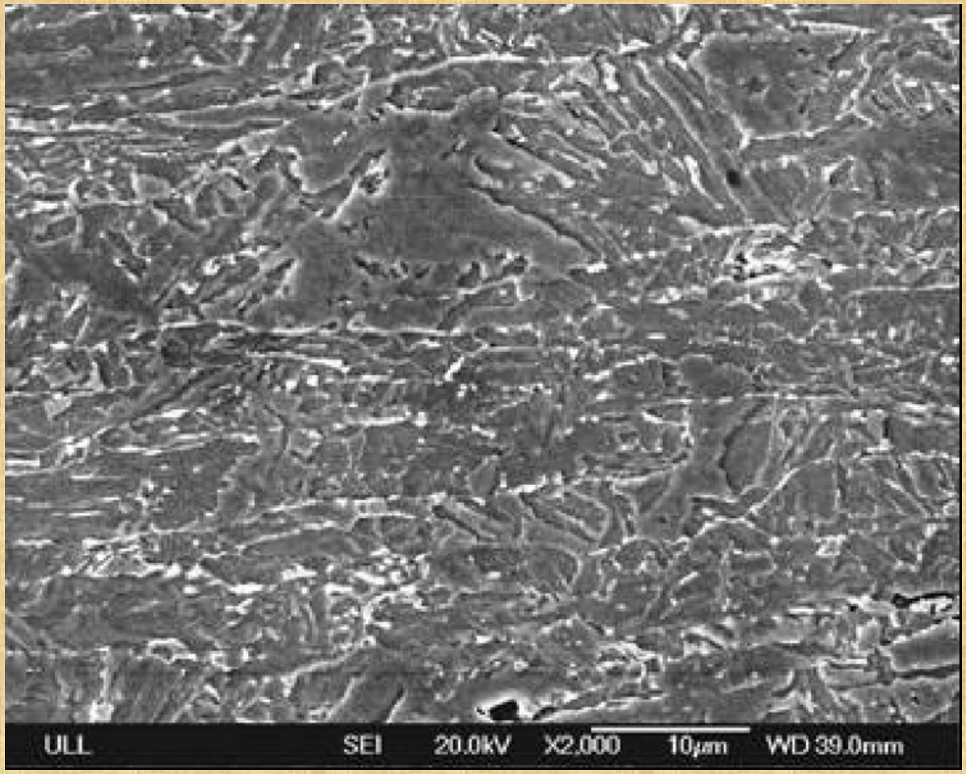
Alloy D (X52/X60 HIC) – Polygonal Ferrite – 100%

SEM Analysis



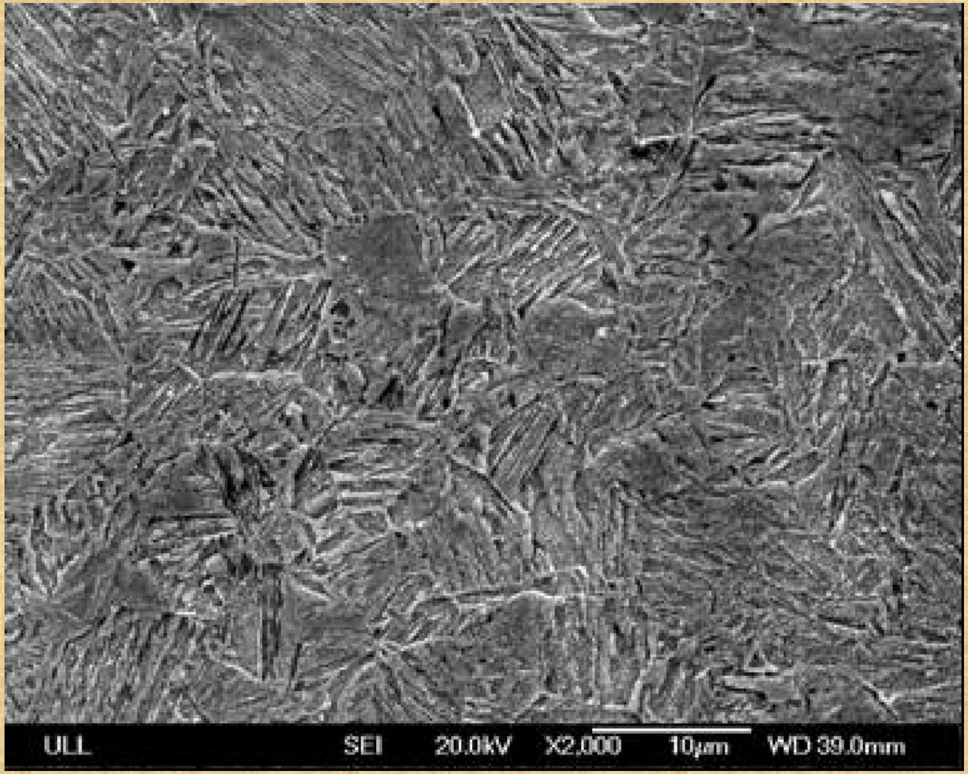
Approach – Details of Microstructural Characterization of Steels Tested

Alloy E (Low C, Abrasion Resistant Steel) – Fine Acicular Ferrite – 100%. SEM Analysis



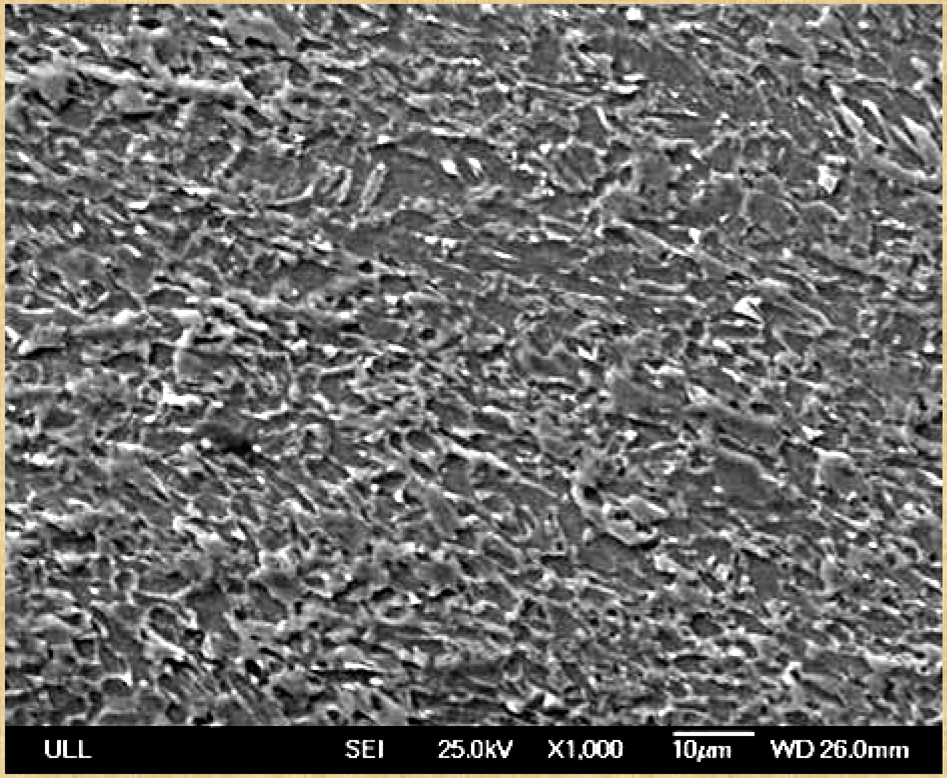
Approach – Details of Microstructural Characterization of Steels Tested

Alloy F (Med C – Hi Alloy, Structural Steel) – Acicular Ferrite – 80%, Lath Type Bainite 20%. SEM Analysis



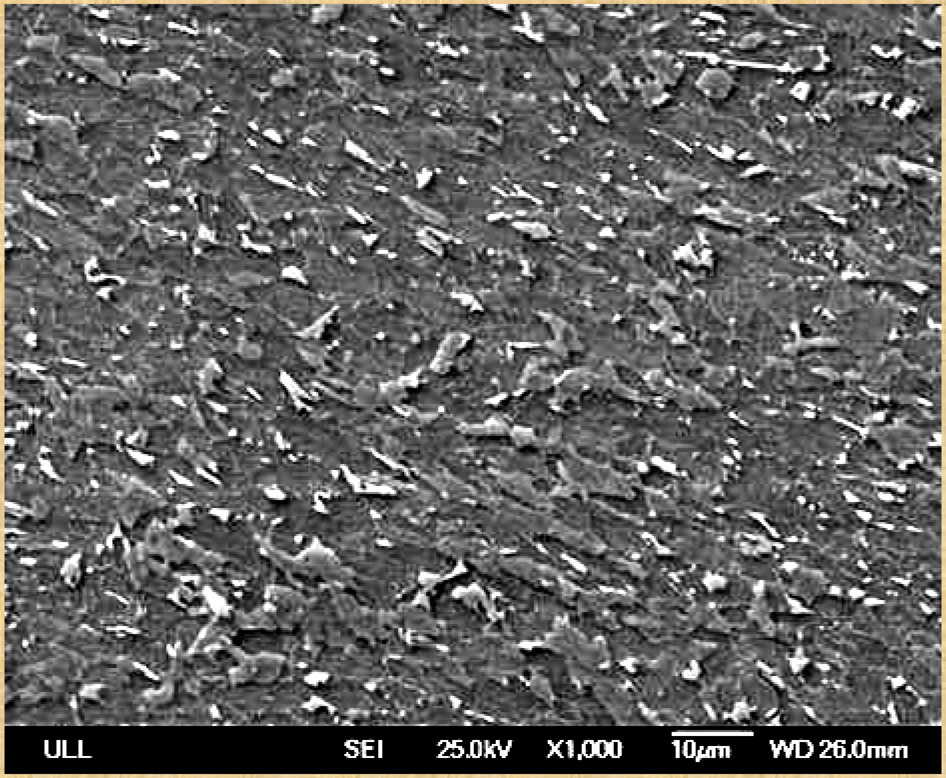
Approach – Details of Microstructural Characterization of Steels Tested

Alloy E (Pipeline Steel) – Fine Acicular Ferrite – 100%. SEM Analysis



Approach – Details of Microstructural Characterization of Steels Tested

Alloy F (Pipeline Steel) – Fine Acicular Ferrite – 70%, Polygonal Ferrite – 30%. SEM Analysis



Approach - Additional Mechanical Property Characterization

- Alloy's B and D's performance across the range of pressures and strain rate in tensile testing appeared to achieve the best performance of the original four tested pipeline steel alloys/microstructures.
- Alloy's B and D were chosen to be further characterized for mechanical properties through fracture toughness and fatigue testing.
- Pressures of 800 and 3000 psi were chosen for the additional characterization work.
- Fracture and fatigue testing were conducted by Sandia National Laboratory.
- In addition, 2 pipeline steels were chosen for fracture testing at Sandia with hydrogen pressure at 3000 psi. This work was done through private sector funding.

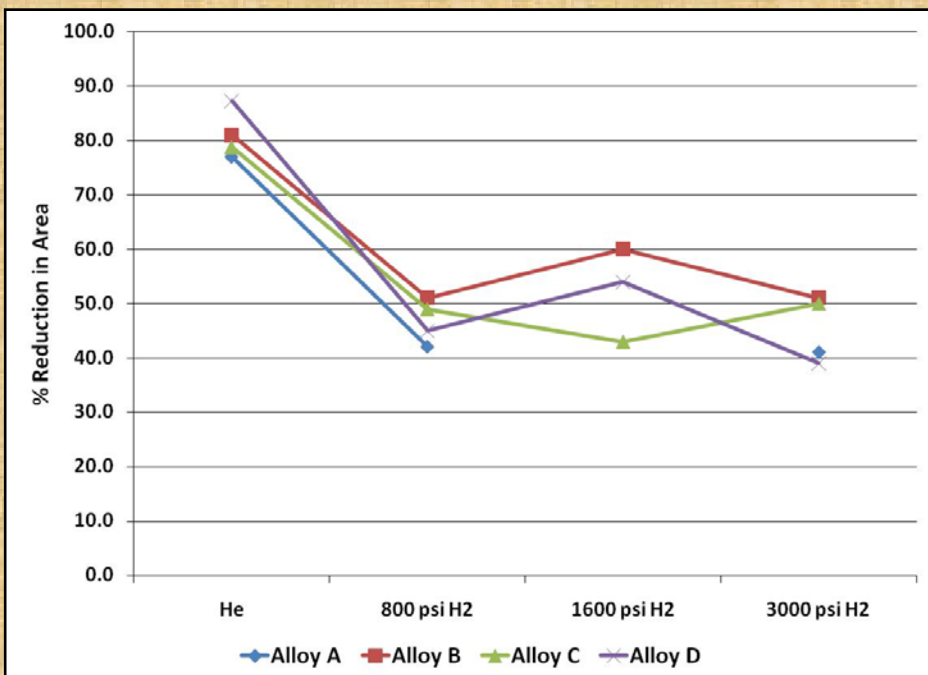
Approach - Additional Mechanical Property Characterization - Sandia Scope of Work

Steel Designation	Testing	# of Fracture Toughness Tests	# of Fatigue Crack Growth Tests
Pipeline Alloy B	800 psi H_2 gas	2	2
	3000 psi H_2 gas	2	2
Pipeline Alloy D	800 psi H_2 gas	2	2
	3000 psi H_2 gas	2	2
Pipeline Alloy E	800 psi H_2 gas	Not in scope of work	Not in scope of work
	3000 psi H_2 gas	2	2
Pipeline Alloy F	800 psi H_2 gas	Not in scope of work	Not in scope of work
	3000 psi H_2 gas	2	Not in scope of work

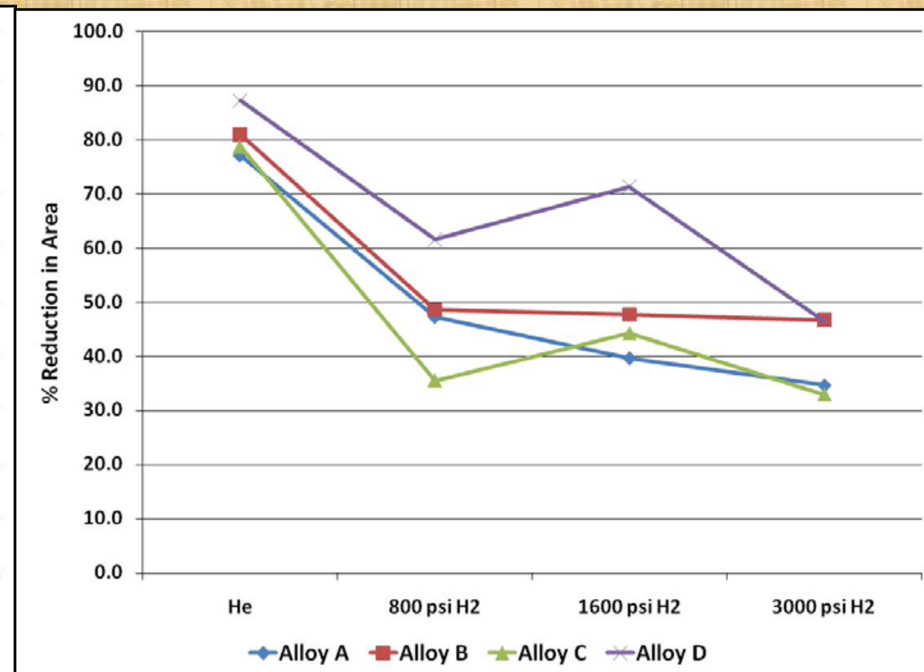
Note: Fracture tests per ASTM E1820, fatigue crack growth testing per ASTM E647. For fatigue testing two R-ratios were evaluated – 0.5 and 0.1 (R is the ratio of the minimum to maximum load applied to the specimen) for Pipeline Alloy B and D. R-ratios of 0.1 evaluated for Pipeline Alloy E.

Technical Accomplishments – *In-situ* Tensile Testing Results in Gaseous Helium and Hydrogen

Reduction in Area, 10^{-4}



Reduction in Area, 10^{-5}



Technical Accomplishments - Fracture Toughness Test Results – Alloy B and D, 800 psi

Alloy B

- Note separation in Alloy B23 fracture.
- Maybe related to microstructural banding of chemically segregated centerline.

Alloy D

Technical Accomplishments - Fracture Toughness Test Results – Alloy B and D, 3000 psi

Alloy B **Alloy D**

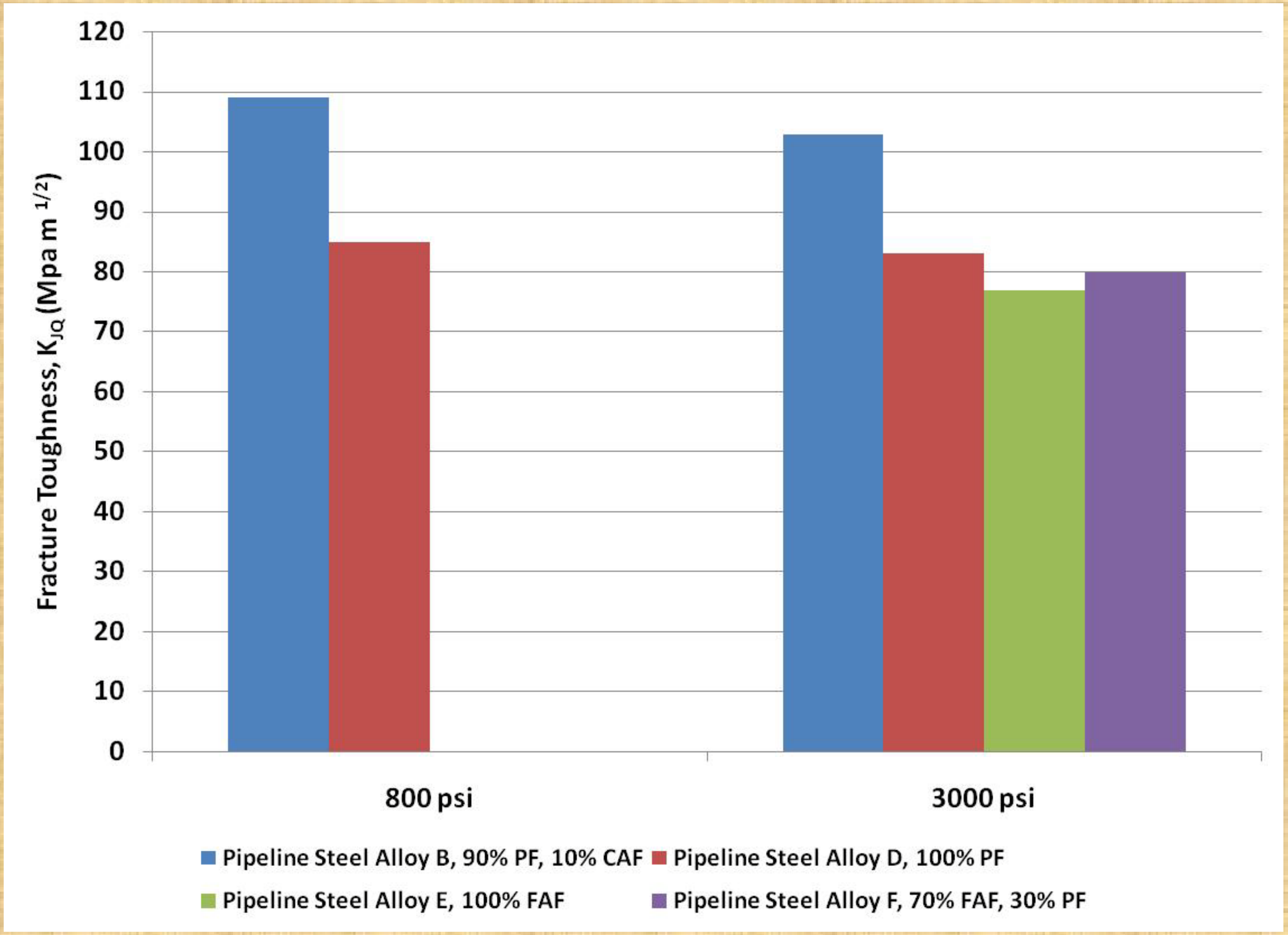
•Note separation in Alloy B22 fracture. Maybe related to microstructural banding of chemically segregated centerline.

Technical Accomplishments - Fracture Toughness Test Results – Pipeline Alloy A (Private Funded), 3000 psi

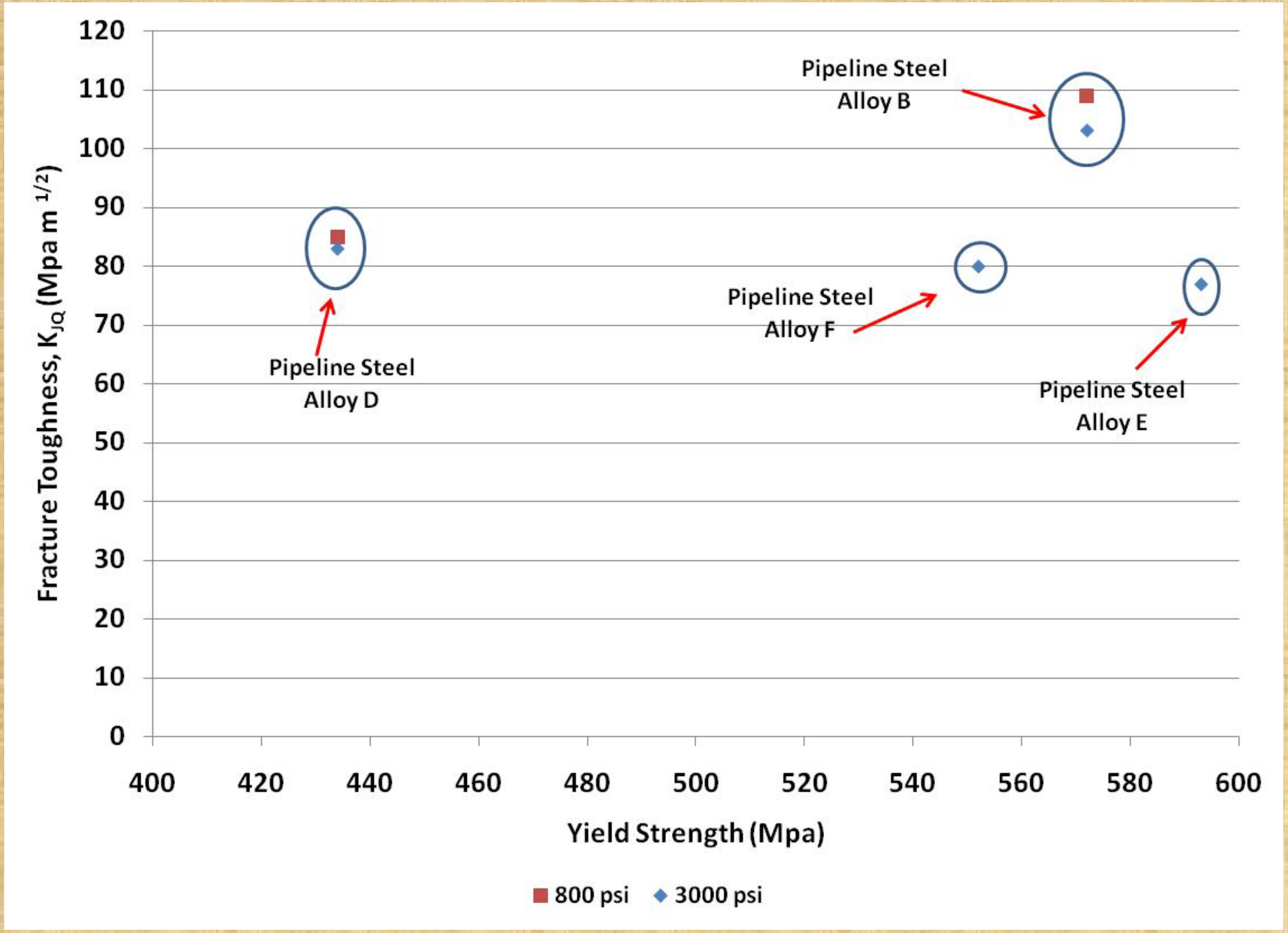
Alloy A

•Note large separation/delamination in Alloy A fracture. Maybe related to microstructural banding of chemically segregated centerline. This needs to be understood better as to cause and it's effect on test results. Alloy A fracture toughness results are not yet complete on this sample.

Technical Accomplishments - Fracture Toughness Test Results – Pipeline Steel Alloy's B, D, E (Private Funded), and F (Private Funded) K_{JIC} vs. Pressure, Average Values

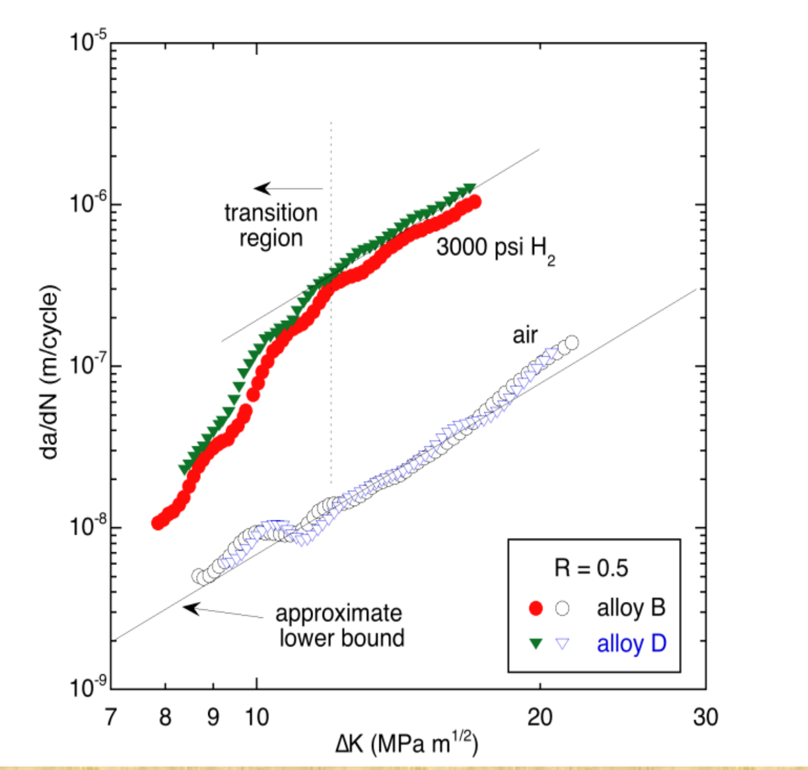


Technical Accomplishments - Fracture Toughness Test Results – Pipeline Steel Alloy's B, D, E (Private Funded), and F (Private Funded), K_{JIC} vs. Actual Yield Strength, Average Values

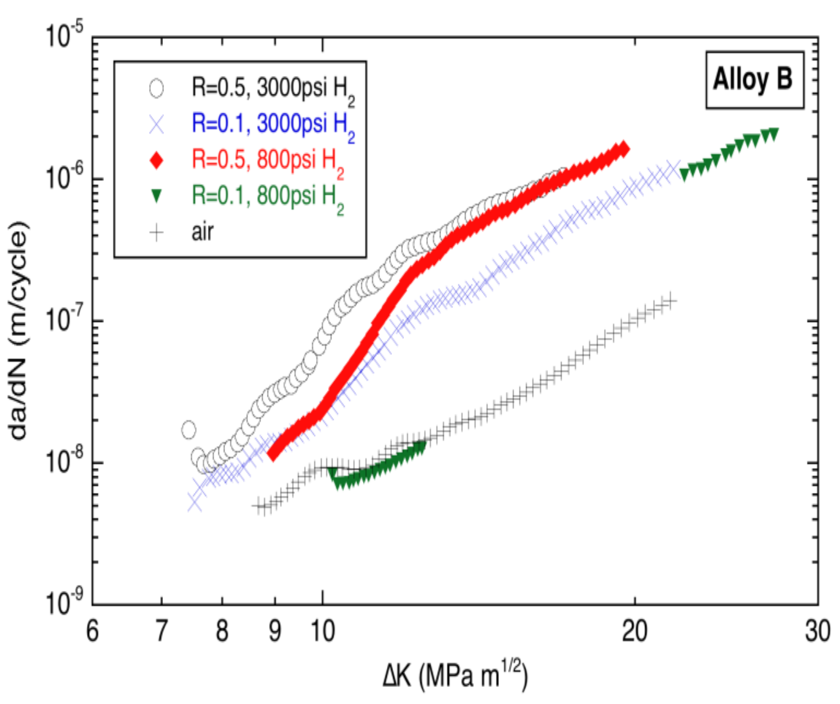


Technical Accomplishments - Fatigue Test Results – Alloy's B and D

FATIGUE CRACK GROWTH OF ALLOY B AND ALLOY D IN GASEOUS HYDROGEN AT PRESSURE OF 3000 PSI, COMPARED TO FATIGUE IN AIR



MEASURED FATIGUE CRACK GROWTH RATES FOR ALLOY B



Technical Accomplishments - Observations from Testing To Date

- Microstructure appears to play a role in resistance to the effect of H2.
  - Polygonal Ferrite/Coarse Acicular Ferrite (Alloy B) appears to be the best performer after tensile and fracture toughness testing, in fatigue testing both microstructures tested the fatigue crack growth rate (FCGR) were similar.
- Increasing yield strength ***does not*** appear to necessarily result in decreased fracture toughness due to the effect of hydrogen in the 800-3000 psi pressure range tested. Microstructure dependent. This may be different than what others have reported at higher pressures.
- R-ratio values of 0.1 and 0.5 performed similarly in the fatigue testing for the two pipeline steel microstructures tested.
- At relatively high ΔK (>12 MPa $m^{1/2}$) the FCGR is about 20 times greater than air, however at lower ΔK the FCGR starts to converge for both air and H_2.
- Understanding the transition between FCGR that are similar to air and those that are 20 times greater is important and necessary.

Technical Accomplishments - Observations from Testing To Date

- Increasing pressure appears to decrease resistance to hydrogen effect. There maybe a potential threshold pressure for a given microstructure.
- Separations/delaminations that occur in some of the testing may bias the results. Detailed examination is required to understand the presence of these vs. microstructural characteristics. ***This is an important point to follow up on in future hydrogen work beyond the scope of this project***.
- Even though there are changes to the reduction in area and fracture toughness how much change is required to deem a microstructure not suitable for service?
- Even though the polygonal ferrite/coarse acicular ferrite microstructure appears to perform the best, does this mean that the other microstructures would not be suitable for service?
- What is the effect of the actual oxide surface layer that is produced in the production of steels? Will it improve the test results? To what magnitude?

Collaborations

- **Partners**
  - ORNL (Federal) provided *in-situ* tensile testing and evaluation of results in high pressure gaseous hydrogen.
  - Coatings partners (Industry) on hold at this time.
  - DGS Metallurgical Solutions (Industry) active as industry technical lead in analysis and interpretation of results.
  - Other industry partners offer expertise as needed on analysis of results along with supply of samples for testing.
- **Technology Transfer**
  - University of Illinois (Academic, DOE H2 project participant) has been given sample from this project for their embrittlement work. Information exchange has been valuable between the two projects
  - Reference Metal Company (Industry) has provided funding and analysis of microstructures.
  - ASME (Industry) has offered input related to needs of B31.12 codes and standards development.
  - Information shared with Sandia National Laboratory (Federal) on steel microstructures and expected performance in gaseous hydrogen environment.
  - DOT/NIST additional fracture and fatigue testing.

Future Work FY11

- **Steels**
  - DOE funded work has concluded. Additional testing is being performed with private sector funding in Phase 2 of the project.
  - Finalize all microstructural characterizations needed for final report. Coordinated through Reference Metals Company.
  - Continued detail analysis and recommendations from data generated in fracture and fatigue testing for final report.
  - All information gathered will be shared with the ASME B31.12 Hydrogen Piping and Pipelines codes and standard committee for review and consideration for incorporation. This will be done through partners ASME and DGS Metallurgical Solutions.
  - Final report to be issued on testing and results completed as part of this DOE funded study.

Future Work (Pending Public and/or Private Funding)

- **Steels –** this project has become the initial stages of developing a broader understanding of the property-microstructure-environmental relationships for steels used in gaseous hydrogen pipelines. There has been much interest by industry and societal standards to expand the scope to include additional pipeline and pressure vessel steels and welds. Initial work (Item 1 and part of Item 2 on matrix next slide) has begun on a Phase 2 with private funding based on the interest level of industry and societal standards organizations. Through private funding and cooperation with a DOT funded project through NIST National Laboratory Phase 2 work will continue.

By filling in the proposed matrix (next slide) of mechanical properties along with data currently or already generated in the past couple of years in the presence of H_2 up to 3000 psi, there will be a characterization/representation of the majority of alloy/microstructure designs used in pipeline steels (base metal) along with some pressure vessel steels currently in service dating to the 1960's along with potential future pipeline construction.

Phase 2 Work Status
(Work Started as Noted, Additional Work Pending Public and/or Private Funding)

Project Code	Grade	Loc	As-received Thickness	Microstructure	C	Mn	P	S	Si	Cu, Ni, Cr, Mo, B	Ti	V	Nb	L - T CVN Testing	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)	S-N Curve, 0.75 YS, R=0.1, 5.0 Hz, 3000 psi air (2 samples)	S-N Curve, 0.75 YS, R=0.1, 5.0 Hz, 3000 psi H2 (2 samples)
A	API - Late 1990's X70 Design	Secat	0.500"	92% PF/8% UB	0.08	1.53	<.018	<.005	0.28	N/A	0.015	0.050	0.061	TBC	2011 Testing - PowerTech	In-progress - PowerTech	In-progress - NIST	In-progess - NIST		
B	API - 2000's X70/X80 w/o Moly Design, Lo Cr	Sandia	0.750"	90% PF/10% CAF	0.05	1.52	<.018	<.005	0.12	<0.60	0.012	NA	0.092	TBC	Completed	Completed	Completed	Completed		
C	API - 2000's X70/X80 w/o Moly Design, Hi Cr	Secat	0.750"	90% PF/10% CAF+ Sm UB	0.04	1.61	<.018	<.005	0.14	<0.75	0.015	NA	0.098							
D	API - Current X80 HIC Design	Secat	0.812"	100% PF	0.03	1.14	<.018	<.005	0.18	<0.60	0.014	NA	0.084	TBC	Completed	Completed	Completed	Completed		
Secat E	Structural 100 KSI Design	Secat	0.500"	100% AF	0.08	1.71	<.018	<.005	0.22	<0.85	0.038	NA	0.044							
Secat F	400 BHN Abrasion Resistant Design	Secat	0.500"	80% AF/20% Lath Type Bainite	0.15	1.42	<.018	<.005	0.42	<0.85	0.035	NA	0.014							
Sandia E	API - 2000's X70/X80 w Moly Design	Sandia	~0.470"	100% FAF	0.06	1.70	<.018	<.005	0.15	<0.120	0.015	NA	0.09	TBC	2011 Testing - PowerTech	In-progress - Sandia	In-progress - NIST	In-progress - Sandia		
Sandia F	API - 2000's X70/X80 w/o Moly Design	Sandia	~0.470"	30% PF/70% FAF	0.06	1.65	<.018	<.005	0.15	<0.100	0.015	NA	0.09	TBC	2011 Testing - PowerTech	In-progress - Sandia	In-progress - NIST	In-progress - NIST		
G	API - 1980's X70 Alloy Design	KM	0.375"	PF/P (10-20%),TBD	.117	1.507	?	?	?		?	?	?	TBC	2011 Testing - PowerTech	2011 Testing - PowerTech				

Color Coding for Microstructure
- Green - Done and makes sense
- Yellow - Done but still needs clarification
- Red - Steel in hand, but micro work to do
- White - no steel available

TBC - To Be Completed

N/A - Not Intentionally Added

Color Coding for Testing
- Blue = Completed Testing
- Green = Funded Testing In-progress
- Yellow = Funded 2011 Testing
- Red = Proposed pending funding
- White - No DOE money to finish
- Orange = Testing should be completed by January 2011

Phase 2 Work Status
(Work Started as Noted, Additional Work Pending Public and/or Private Funding)

Project Code	Grade	Loc	As-received Thickness	Microstructure	C	Mn	P	S	Si	Cu, Ni, Cr, Mo, B	Ti	V	Nb	L - T CVN Testing	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)	S-N Curve, 0.75 YS, R=0.1, 5.0 Hz, 3000 psi air (2 samples)	S-N Curve, 0.75 YS, R=0.1, 5.0 Hz, 3000 psi H2 (2 samples)
H	API - 1960's X52 Alloy Design	KM	0.312"	70% PF/30% P	0.26	1.01	0.02	0.017	0.036	<0.20	0	0	0	TBC	2011 Testing - PowerTech	In-progress - PowerTech	In-progress - NIST	In-progress - NIST		
I	API - Early 1990's X70 Design	Sandia	0.450"	85-90% PF/10-15% P	0.08	1.50	<.018	<.005	0.3	NIA	0.015	0.070	0.050	TBC	2011 Testing - PowerTech	In-progess - PowerTech	In-progess - NIST	In-progess - NIST		
J	API - 1990's/2000's X52 Alloy Design	Sandia	0.500"	PF/P (10%) TBD	0.06	0.87	0.011	0.006	0.12	NIA	0	0	0.03	TBC	2011 Testing - PowerTech	Completed		Completed		
K	PV - ASTM A516 Gr70 w/o microalloy	TBD	TBD	PF/P (40+%) TBD	0.23?	1.20?	<.018?	<.005?	.30?		.001?	NA?	NA?							
L	PV - ASTM A516 Gr70 with microalloy	TBD	TBD	PF/P (40+%) TBD	0.23?	1.20?	<.018?	<.005?	.30?		.001?	NA?	.02?							
M	API X70 - Pipeline Long Seam Welds	Secat		As-cast TBD	?	?	?	?	?		?	?	?							
N	API - Pipeline Girth Welds	TBD	TBD	As-cast TBD	?	?	?	?	?		?	?	?							
P	Induction Bend Comparison X52	Air Liquide	TBD	TBD - Induction vs. Base	?	?	?	?	?		?	?	?							

Color Coding for Microstructure
- Green - Done and makes sense
- Yellow - Done but still needs clarification
- Red - Steel in hand, but micro work to do
- White - no steel available

TBC - To Be Completed

NIA - Not Intentionally Added

Color Coding for Testing
- Blue = Completed Testing
- Green = Funded Testing In-progress
- Yellow = Funded 2011 Testing
- Red = Proposed pending funding
- White - No DOE money to finish
- Orange = Testing should be completed by January 2011

Project Summary

Relevance: Establish potential suitability of steel pipelines for gaseous hydrogen service.

Approach: Utilizing commercially available existing pipeline steels and industry expertise generate relevant mechanical property data vs. microstructure in the presence of high pressure gaseous hydrogen.

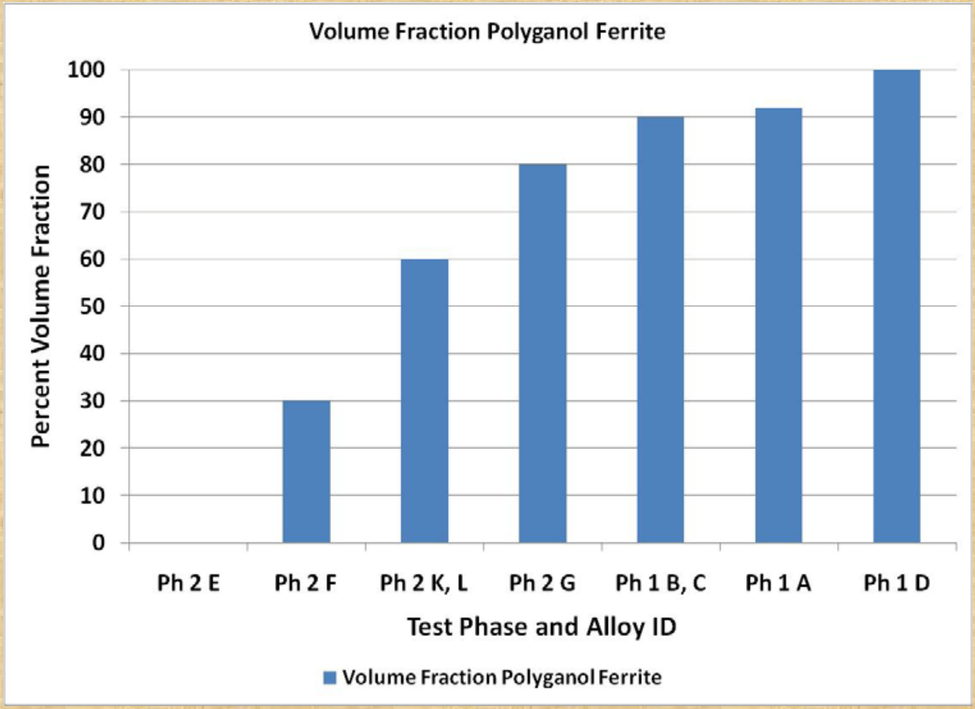
Technical Accomplishments and Progress: Demonstrated that two of four commercially available pipeline microstructures have potential to minimize hydrogen effect at pressure. Demonstrated that one of the final two performed better in fracture toughness testing. Demonstrated that microstructure does play a role in performance in gaseous hydrogen in pressure range tested. Fatigue testing using 2 different pressures and R-ratio values did not vary significantly between the two final microstructures tested. Microstructural characterization of 8 different alloys completed.

Technology Transfer/Collaborations: Active participation with other DOE and DOT hydrogen research funded national laboratories and Universities along with utilization of available industry experts.

Proposed Future Research: Finalize analysis of data and submit final report. Additional Phase 2 work has started in collaboration with DOT funded project along with private sector. All data generated along with additional information generated will be shared with ASME B31.12.

Technical Back Up Slides

Illustration of Microstructure Testing in Phase 1 (DOE Funded)/Phase 2 (DOT/Private Sector Funded)



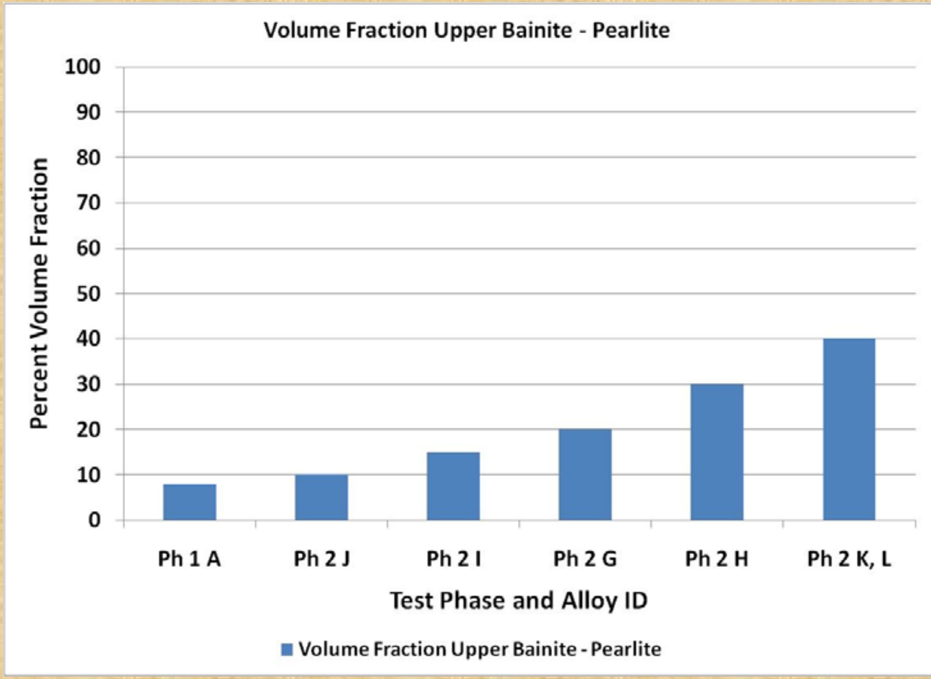


Illustration of Microstructure Testing in Phase 1 (DOE Funded)/Phase 2 (DOT/Private Sector Funded)