

Materials Solutions for Hydrogen Delivery in Pipelines

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Merit Review and Peer Evaluation Meeting
Arlington, VA

Project ID –
PD_50_Stalheim

Overview

Timeline

- Project start date: 05/2005
- Project end date: 09/2011
- Percent complete: 40%

Budget

- Total project funding
 - \$1650K (DOE share)
 - \$1110K (contractor share)
- Funding for FY 07: \$173K
- Funding for FY 08: \$113K
- Funding for FY 09: \$240K

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:

- 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 H₂ is **not well understood**
- Effect of steel metallurgical microstructures on hydrogen embrittlement in a high pressure dry gaseous H₂ environment are **not known**
- Effectiveness of metallic and non-metallic coatings on minimizing H₂ 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 will be further evaluated with fracture toughness and fatigue testing in high pressure gaseous hydrogen. The other two alloys may be evaluated at a later date.
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.
September 09	Milestone: Complete 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.

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.

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 at ORNL complete (Main focus for this presentation)
 - Two strain rates - 1×10^{-4} , 1×10^{-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

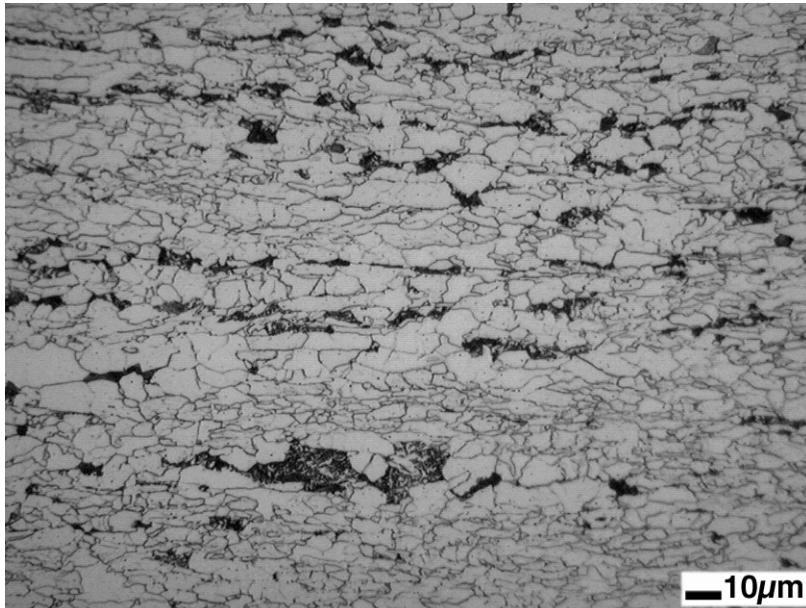
Progress To Date

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

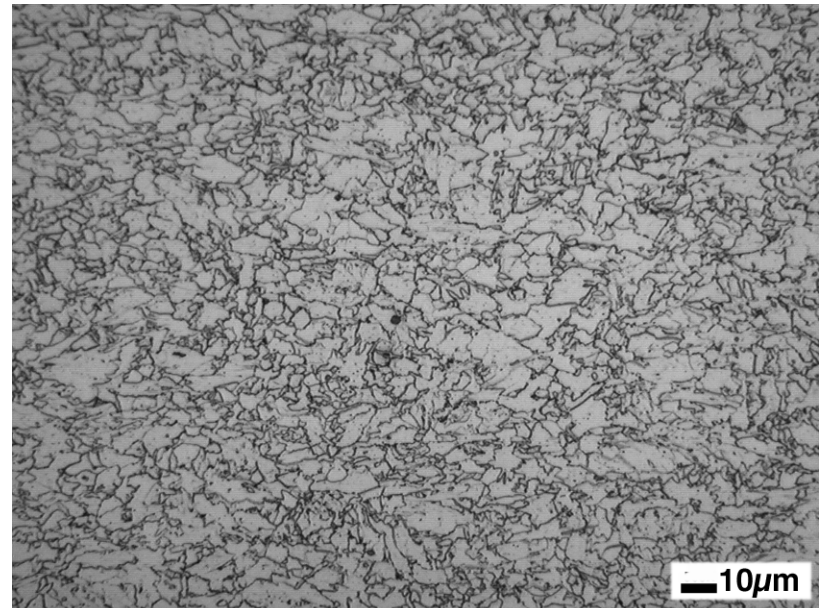
- One is low carbon-high alloy capable of producing 100% bainite or 100% martensite microstructures (dependant on processing) with good toughness
- Second is medium carbon-high alloy capable of producing 100% bainite or 100% martensite microstructures (dependant on processing) with good toughness

Approach - Microstructures Tested

**Alloy A (X70) – Ferrite/Pearlite
(Pearlite ~ 6.5% average)**

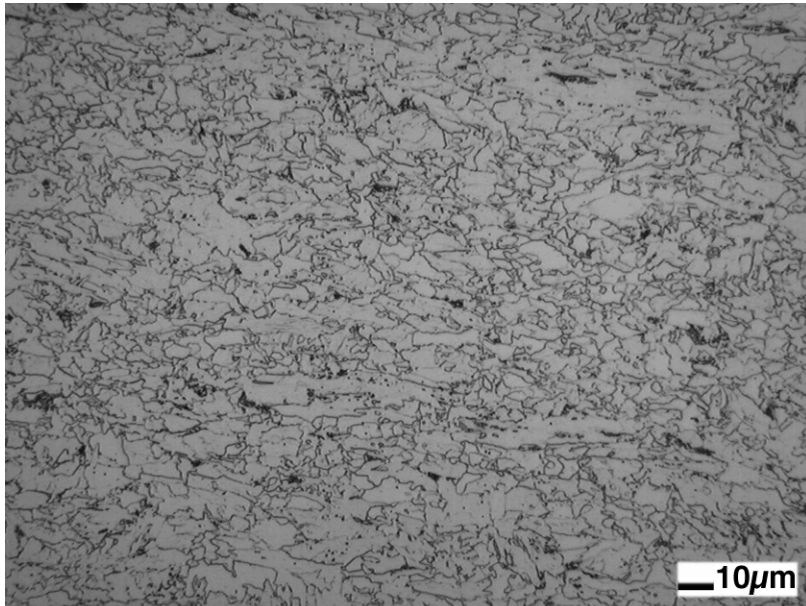


**Alloy B (X70/X80) – Ferrite/Acicular
Ferrite (Volume Fraction – TBD)**

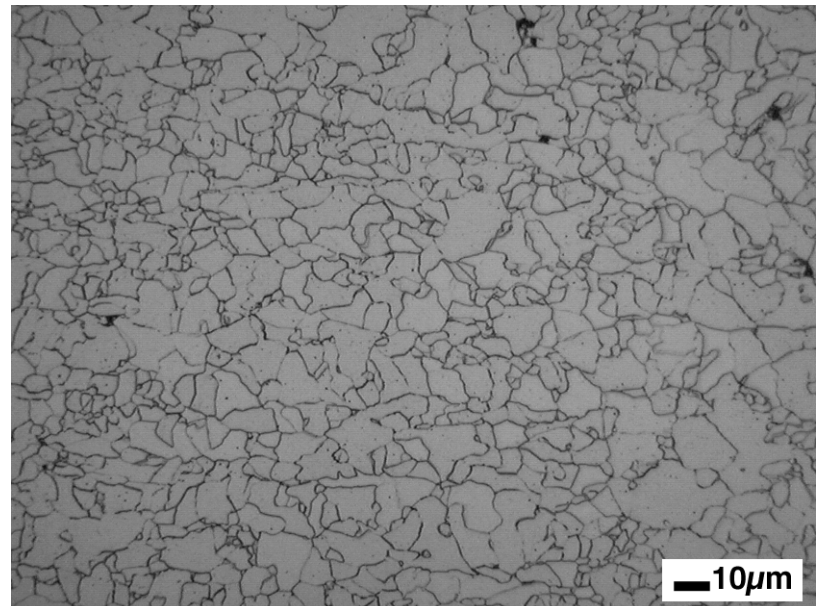


Approach - Microstructures Tested

**Alloy C (X70/X80) – Ferrite/Acicular
Ferrite /Sm Pearlite (Vol Frac AF – TBD)
(Pearlite < 3%)**

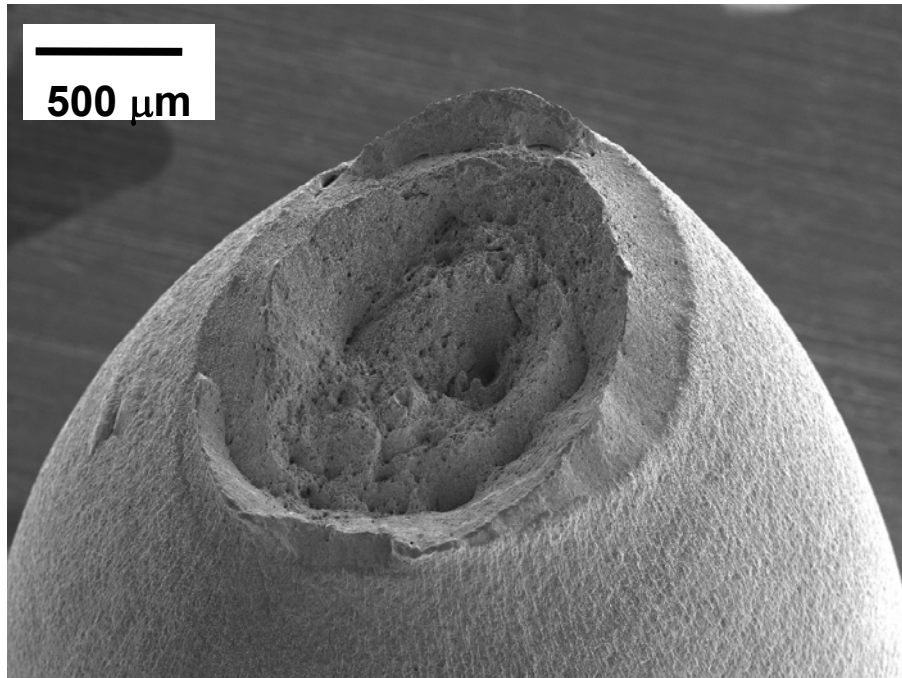


**Alloy D (X52/X60 HIC) – Ferrite/Acicular
Ferrite (Volume Fraction – TBD)**

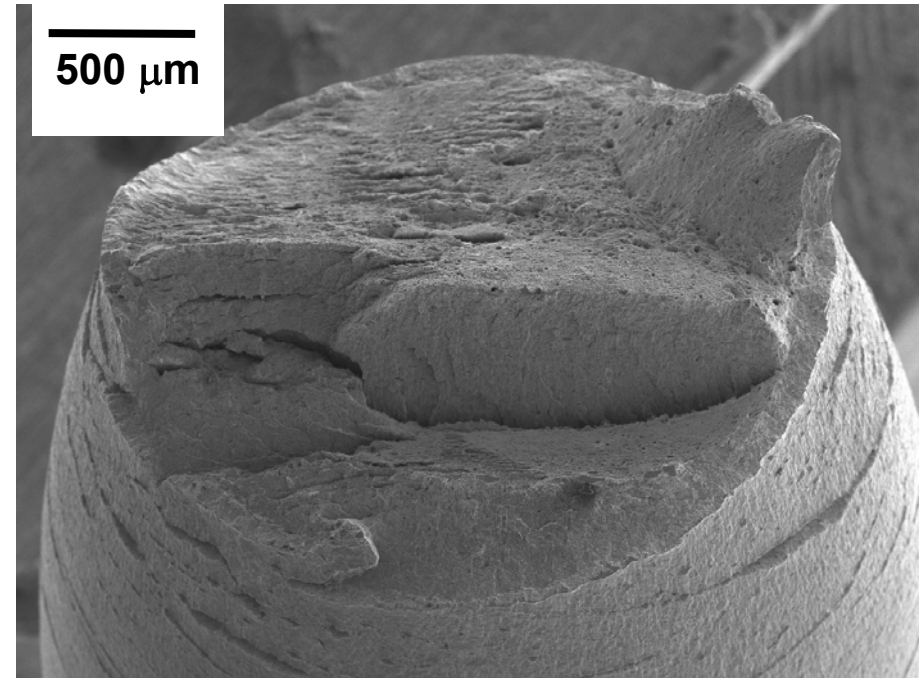


Technical Accomplishments – Alloy A Shows Loss of Ductility in H₂ Atmosphere

•800 psi He, 1×10^{-4} /sec

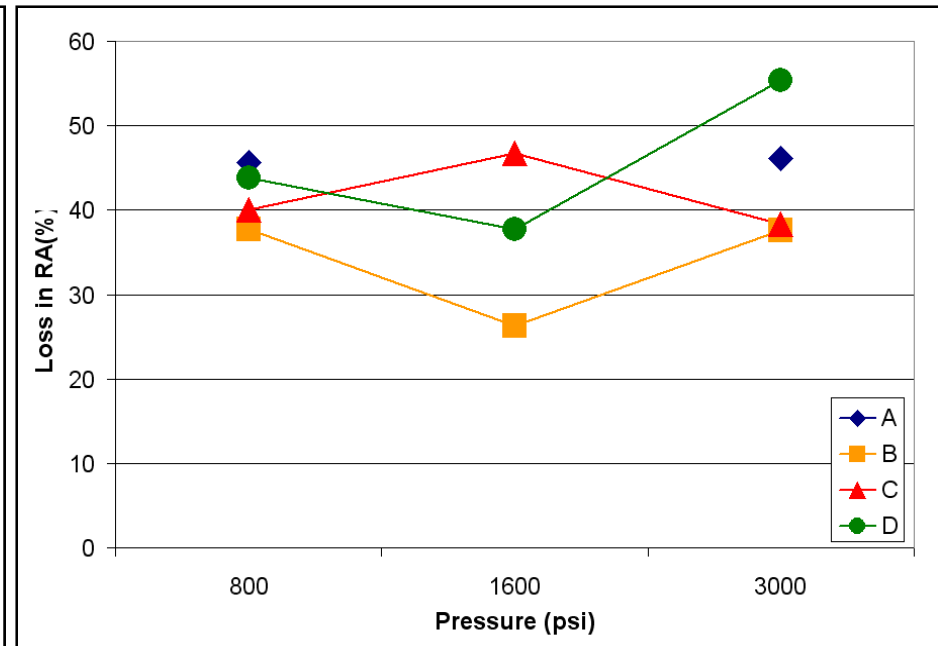
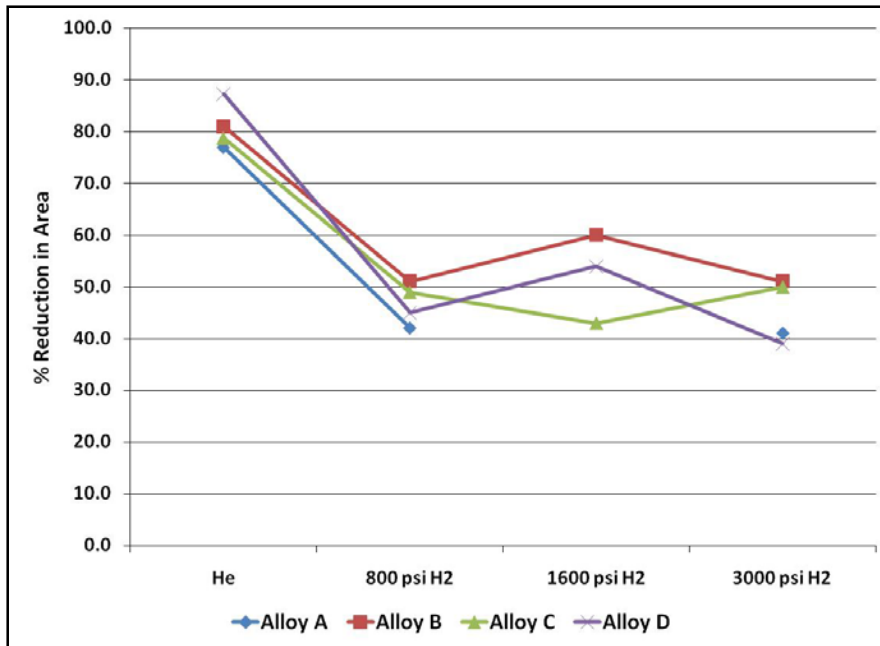


•800 psi H₂, 1×10^{-4} /sec



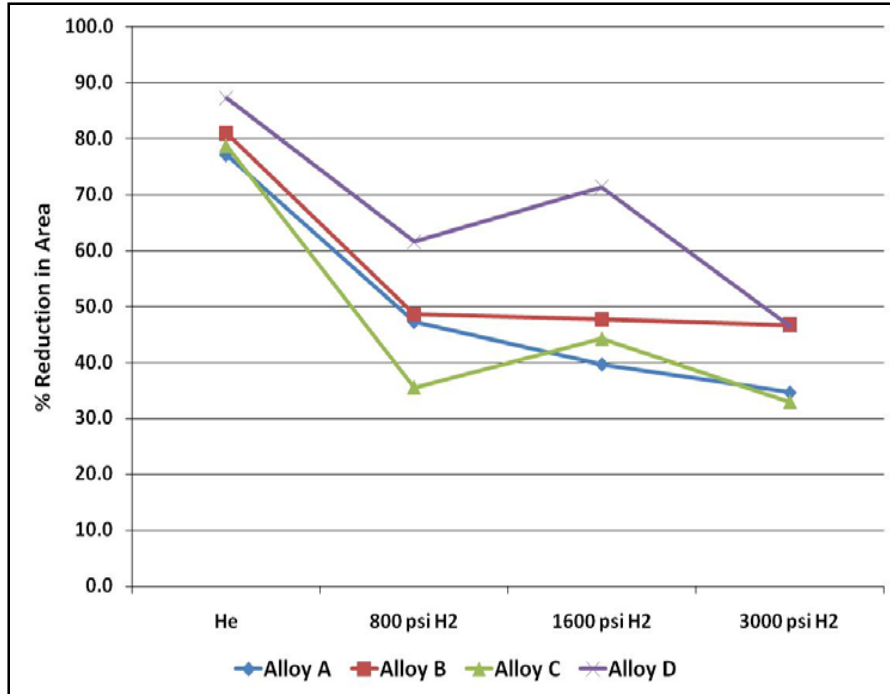
Technical Accomplishments – *In-situ* Tensile Testing Results in Gaseous Hydrogen

Reduction in Area, 10^{-4} Loss in Reduction in Area, 10^{-4}

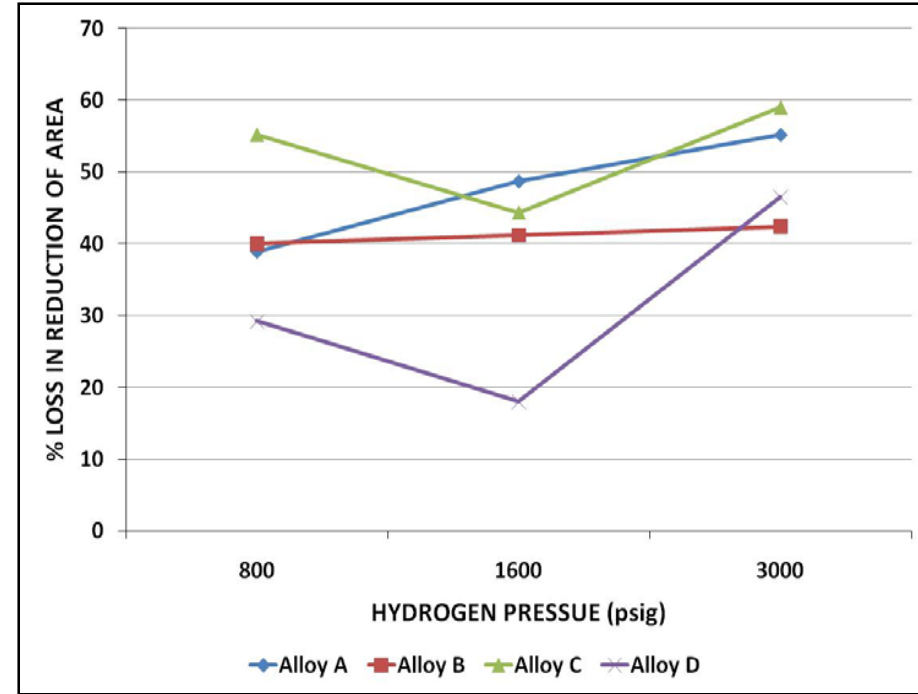


Technical Accomplishments – *In-situ* Tensile Testing Results in Gaseous Hydrogen

Reduction in Area, 10^{-5}



Loss in Reduction in Area, 10^{-5}

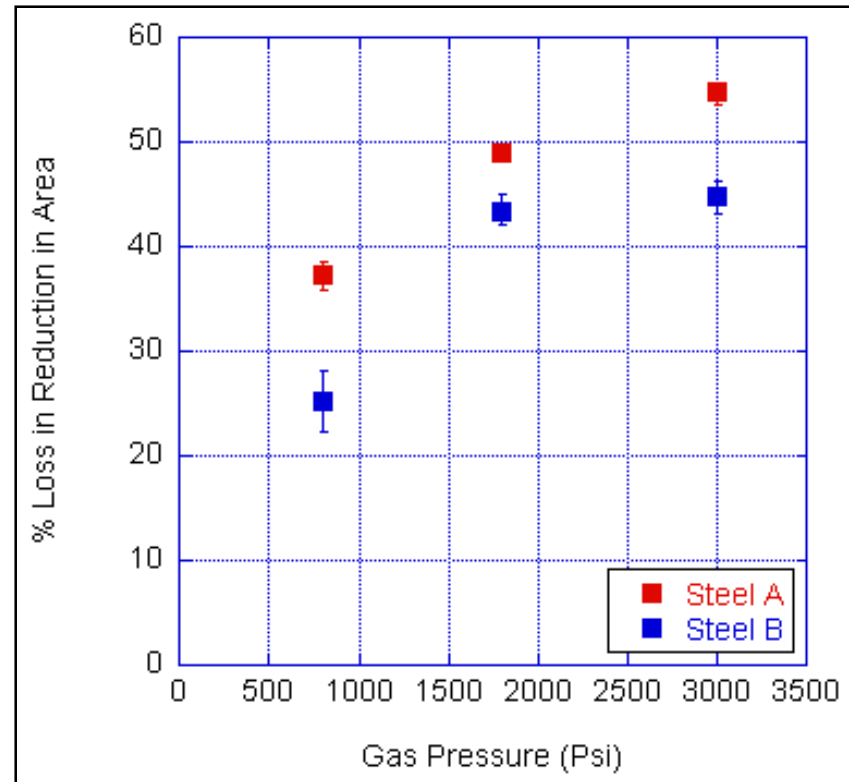


Technical Accomplishments - Additional Tensiles Tests Performed on Steels A and B

% Loss in Reduction in area is defined as

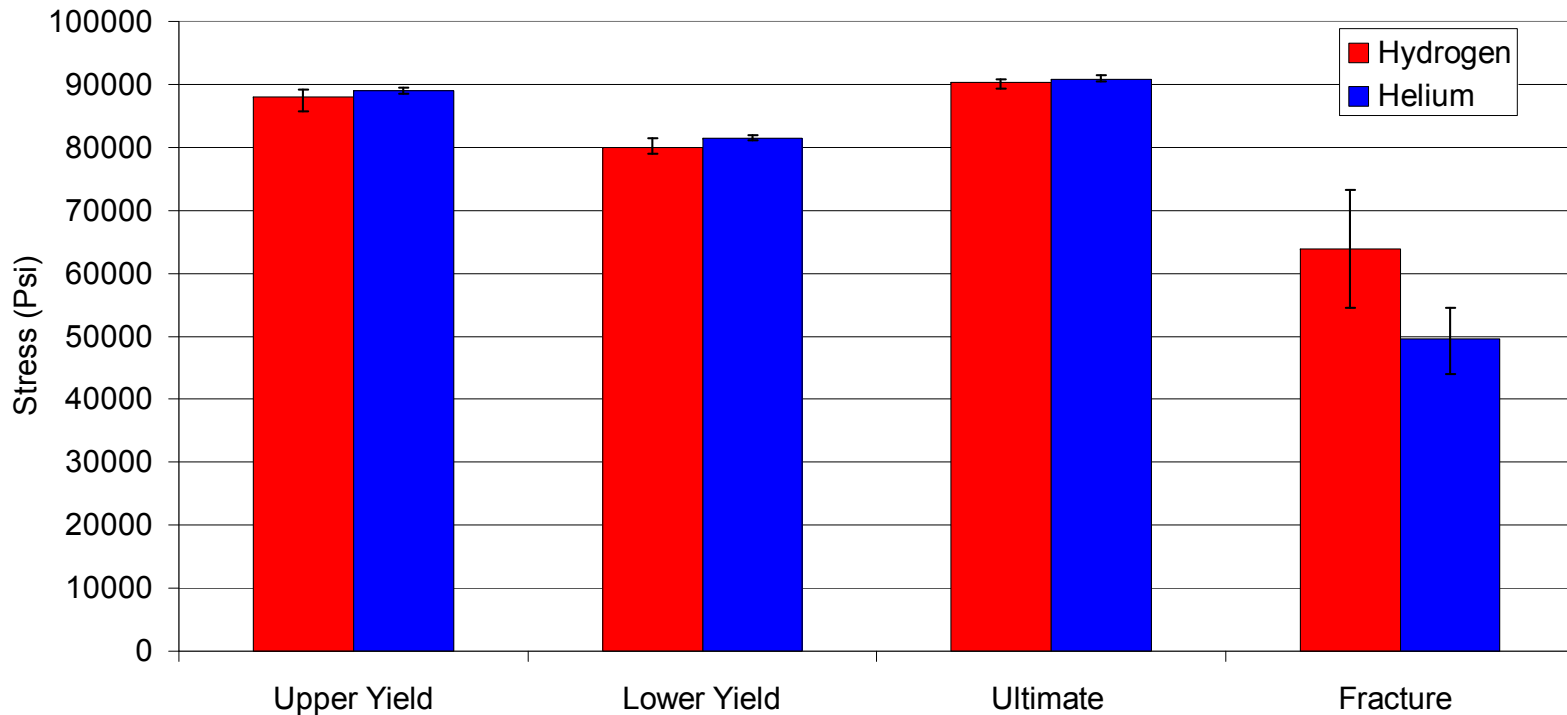
$$\left(\frac{\%RA(He) - \%RA(H_2)}{\%RA(He)} \right) * 100$$

Observed % loss in RA is lower for Steel B at all pressures



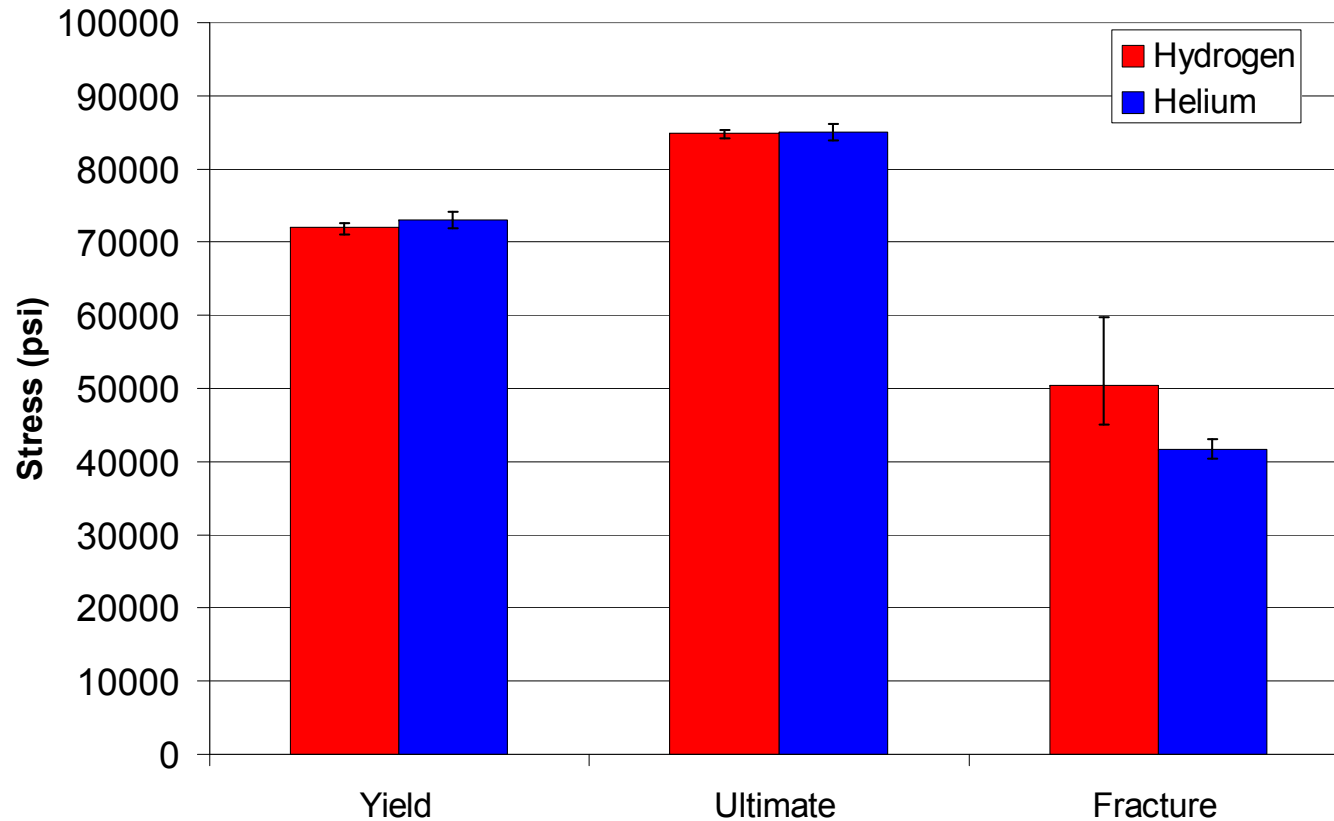
•Pre-yield Strain rate = 1×10^{-5} /sec

Technical Accomplishments - Yield and Ultimate Strengths of Alloy A are Not Affected by the Hydrogen Atmosphere



- Fracture stress is affected by the presence of hydrogen

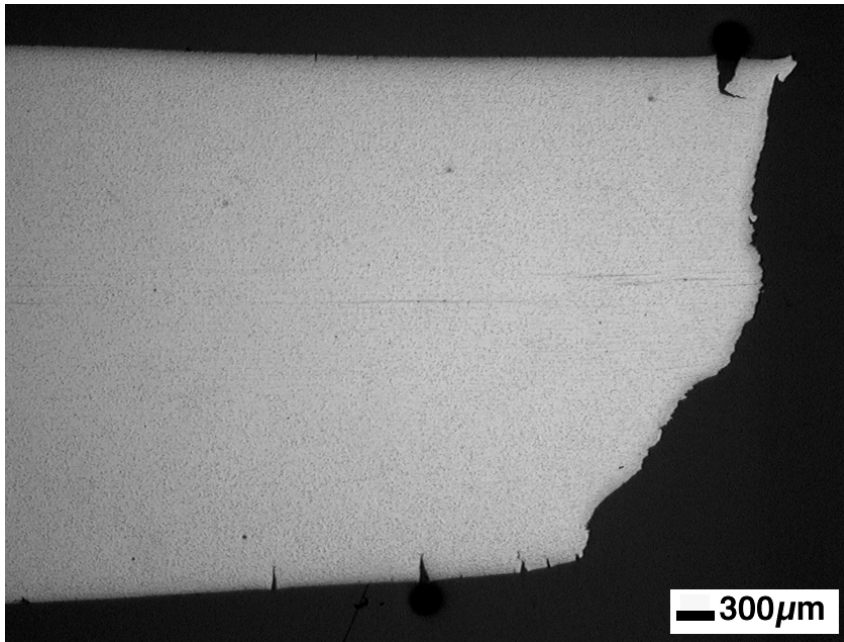
Technical Accomplishments -Yield and Ultimate Strengths of Alloy B Not Affected by Hydrogen



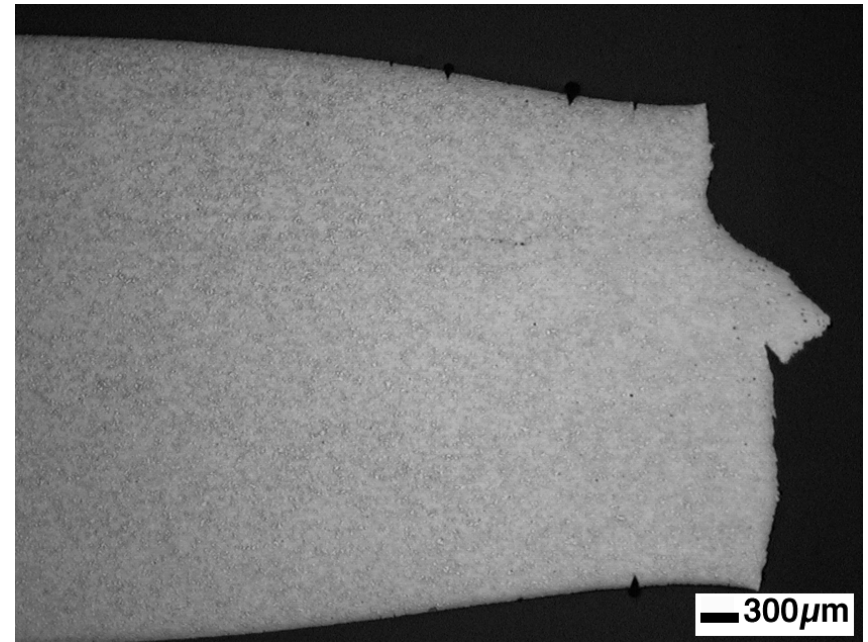
- Fracture stress is affected by the presence of hydrogen

Technical Accomplishments - Optical Images of Cross-section of Failed Specimens Show Presence of Radial cracks

•3000 psi H₂, 1x10⁻⁵/sec



•Alloy A



•Alloy B

Technical Accomplishments - Questions/Comments from Initial Testing

- Microstructure appears to play a role in resistance to the effect of hydrogen (Ferrite/Acicular Ferrite appears to be the best performer, Alloy B and D in particular)
- Even though there are changes to the reduction in area, how much change is required to deem a microstructure not suitable for service?
- Increasing pressure appears to decrease resistance to hydrogen effect. There maybe a potential threshold pressure for a given microstructure.
- Effect of strain rate and hydrogen pressure is complex and maybe dependent on microstructure.

Technical Accomplishments - Questions/Comments from Initial Testing

- Even though the ferrite/acicular ferrite microstructure appears to perform the best, does this mean that the other ferrite/pearlite microstructure would not be suitable for service?
- Are the reduction in area values for Alloys C and D correct at 800 and 1600 psi? Are there some other data points that should be revisited? Verification testing will be required.
- What is the effect of the actual oxide surface layer that is produced in the production of steels? Will it improve the reduction in area results for all? 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 macrostructures and expected performance in gaseous hydrogen environment.

Future Work FY09

- **Steels**

- Validation of select reduction in area values of Alloy's B, C and D at pressure in hydrogen at ORNL.
- Further testing and evaluation of Alloy's B and D for service in high pressure hydrogen, subcontracted to Sandia National Laboratory
 - Fracture mechanics testing at 800 psi and 3000 psi
 - JR Curves per ASTM 1820
 - Fatigue crack growth testing at 800 psi and 3000 psi
 - da/dn curves vs. ΔK per ASTM 647
- Final microstructural characterizations to determine volume fractions of pearlite, ferrite, bainite, etc. in Alloy's A, B, C, and D. Coordinated through Reference Metals Company.
- 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.

Future Work (Pending Funding)

- **Steels**

- *In-situ* tensile testing of alternative alloy/microstructure designs already down selected from Task 2 along with another acicular ferrite microstructure steel, verify results.
- Complete further tests Alloys A, C and D at pressure in hydrogen at ORNL using *in-situ* tensile testing to obtain statistical variation in results
- Characterize the effect of one impurity gas on properties evaluated using *in-situ* tensile testing
- Final microstructural characterizations to determine volume fractions of pearlite, ferrite, bainite, etc. in Alloys A, B, C, and D
- Determine, if possible suitability of ALL alloy's tested for hydrogen service
 - Volume fractions of microstructure thresholds
 - Pressure thresholds
 - Other factors (industrial surface oxide, etc.)

Future Work (Pending Funding)

- **Steels**

- Understand and evaluate values achieved with different strain rates used in the *in-situ* testing
- Complete microstructural characterization of down-selected steels after exposure to hydrogen to understand the effect of microstructure on embrittlement
- Evaluate *in-situ* fatigue and fracture mechanics testing of commercial pipeline steels Alloy's A and C along with alternative microstructures from Task 2.
- Add alloy with higher volume fraction of pearlite (~ 20-30%) to the *in-situ* testing to evaluate volume fraction thresholds (represents older 1950-1980's pipeline metallurgy)
- Additional 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.

- **Economic Analysis**

- Recommend steel and coating systems for implementation
- Evaluate economic impact of suggested materials systems

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 microstructures have potential to minimize hydrogen effect at pressure.

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

Proposed Future Research: Validation of previous *in-situ* tensile testing data. Further evaluation of two pipeline steels fracture mechanics and fatigue characteristics in high pressure gaseous hydrogen. Finalize microstructure characterization. All data generated will be shared with ASME B31.12. Additional evaluation for suitability for service, additional testing of alternative microstructures, and economic analysis will be dependent on future funding. Any additional information generated will be shared with ASME B31.12.

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