III.15 Materials Solutions for Hydrogen Delivery in Pipelines

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Subcontractors:

- Evraz North America (formally Oregon Steel Mills), Portland, OR
- Schott North America, Duryea, PA
- Chemical Composite Coatings Int'l, LLC, Alpharetta, GA
- Advanced Technology Corporation (ATC), Oak Ridge, TN
- Columbia Gas of Kentucky, Lexington, KY
- ASME Standards and Technologies LLC, New York, NY
- DGS Metallurgical Solutions, Inc, Vancouver, WA
- Hatch Mott MacDonald, Monroe, LA
- Reference Metals Company, Bridgeville, PA

Start Date: May 2005
Projected End Date: September 2011

Objectives

Overall goal of the project is to develop materials technologies that would enable minimizing the problem of hydrogen embrittlement associated with the high-pressure transport of hydrogen:

- The most important aspect of the project is to identify base steel compositions/microstructures 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.
- Understand the economics of implementing new technologies.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines
(K) Safety, Codes and Standards, Permitting

Technical Targets

The objective of the project is to develop materials technologies that would enable minimizing the problem of hydrogen embrittlement associated with the high-pressure transport of hydrogen through pipelines. Such materials technologies in combination with cost-effective excavation and fabrication technologies will facilitate reducing the capital cost of pipelines. Insights gained from these studies will be applied toward the design and construction of hydrogen delivery systems that meet the following DOE 2017 hydrogen delivery pipeline transmission targets:

- Reliability (relative to hydrogen embrittlement concerns and integrity; the first two bullet points are of main importance to the project):
  - Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen. Based on results to date, there appears to be commercially available pipeline microstructures that perform better than others in the presence of gaseous hydrogen.
  - Evaluate hydrogen embrittlement characteristics of existing alternative commercially available steels under high-pressure hydrogen.
  - Develop alternate alloys and evaluate hydrogen embrittlement.
  - Develop coatings to minimize dissolution and penetration of hydrogen and evaluate hydrogen embrittlement in coated alloys.
- Pipeline Transmission Total Capital Cost ($M/Mile): $0.49 for 16" outside diameter transmission pipeline
  - Financial analysis and incorporation into codes and standards.

Accomplishments

Accomplishments to date are as follows:

- Four commercially-available pipeline steels along with two commercially-available alternative steels have been down-selected for initial study of their hydrogen embrittlement characteristics under high pressure hydrogen.

- The four commercially-available pipeline steel microstructures and mechanical property data have been characterized.
- Commercial X70 pipeline welds available.
- Two traditional screening tests have been explored.
- In situ Automated Ball Indentation (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 Oak Ridge National Laboratory (ORNL) complete on the four pipeline steels
  - Two strain rates - $1x10^{-4}$, $1x10^{-5}$, hydrogen vs. helium, three pressures – 800 psi, 1,600 psi, 3,000 psi, total initial tests = 48, additional validation testing = 10, additional statistical testing of alloy A and B.
- The in situ tensile testing was evaluated and used to screen the four pipeline steels for further fracture and fatigue testing. From this evaluation, two of the pipeline steels were selected for further testing.
- Fracture and fatigue testing have been completed in hydrogen for the two selected pipeline steels. Gaseous hydrogen test pressures for fracture and fatigue testing were bracketed between 800 and 3,000 psi to represent potential transmission pressures. Fatigue testing utilizing two R-ratio values has been explored along with testing in air for comparison purposes.
- Actual construction costs of a pipeline project supplied by Columbia Gas of Kentucky reviewed by the project team.

Note that all work related to coatings has been placed on hold per DOE.

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Introduction

Pipeline transmission is the most economical method for hydrogen delivery in large quantities from the point of generation to point of use. As transmission pressures are increased, steel pipelines that could be used for the transport of hydrogen at low pressures are prone to hydrogen embrittlement at the welds, the heat-affected-zone and/or the base metal regions in 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. The increasing integration of computational techniques with experimental methods has resulted in the development of “designer” materials along with the scientific methodologies for developing customized materials better suited for any given application. New coating materials and coating technologies hold promise in developing barrier coatings to minimize the dissolution and permeation of hydrogen through steels.

The work on this project represents an integrated approach to developing and testing new materials solutions to enable pipeline delivery of hydrogen at high pressures. The scope of the project includes: (1) identification of steel compositions and associated welding filler wires and processes that would be suitable for new pipeline infrastructure or indicate use of existing pipeline infrastructure for transport of hydrogen at requisite high pressures; (2) development of barrier thin film coatings that would minimize the hydrogen permeation in the current natural gas pipelines; and (3) understanding the cost factors related to the construction of new pipelines and modification of existing pipelines and to identify the path to cost reduction. The team participating in this proposal is lead by SECAT Inc. and includes ORNL, DGS Metallurgical Solutions, Inc., ASME Standards and Technologies, University of Illinois, Schott North America-Regional R&D, Columbia Gas, Chemical Composite Coatings International LLC, Advanced Technology Corporation, EVRAZ North America (formerly Oregon Steel Mills), Reference Metals Company and Hatch Moss MacDonald.

Approach

Achievement of an understanding to the mechanisms of hydrogen embrittlement of commercially-available transmission pipeline steels and welding consumables will involve characterization of the mechanical properties and microstructures in both the absence and presence of high-pressure hydrogen gas. The study of vintage pipeline steels along with current pipeline steel technology and potential alternative alloy designs will help determine the optimum mechanical properties and microstructure required to operate in a high pressure hydrogen gas environment. Both in situ and ex situ methods will be used to study the effect of hydrogen gas under pressure on microstructural and mechanical properties. Thermokinetic modeling and microstructural characterizations will be used in the analysis.

In addition, glass and oxide coatings to impede the permeation of hydrogen gas to the steel will be explored, developed and tested in the presence of high-pressure hydrogen gas. Coated steel mechanical properties in the presence of high-pressure hydrogen gas will be tested and compared to uncoated specimens. Successful coatings will be tested for resistance to damage related to required pipeline operational non-destructive testing techniques.

Factors related to materials and construction costs are incorporated into the project. This understanding will allow for recommendations for optimum material selections and fabrication of transmission pipeline systems suitable for high pressure hydrogen gas transport.

Results

Four commercially-available pipeline steels and two commercially-available alternative steels have been down-selected for initial study of their hydrogen embrittlement under high-pressure hydrogen. The compositions of these steels are shown in Table 1. It is anticipated that a study of these steels would be representative of advanced steels and would point to additional compositions that need to be studied in order to develop an appropriate relationship between compositions, structure, and hydrogen embrittlement characteristics.

Mechanical properties, microstructural characterizations, thermokinetic modeling, ex situ high-pressure hydrogen testing, 2,000 psi testing at ATC, corrosive National Association of Corrosion Engineers (NACE) testing and in situ of the four pipeline alloys have been completed. All of these results have been reported prior. All of this testing has shown that microstructural differences cause different behaviors in the presence of hydrogen. Some of the behaviors appear to be positive while others may appear negative.

Glass coating development has been progressing and has been reported in previous reports. In addition, Actual costs to construct a natural gas pipeline were supplied by Columbia Gas of Kentucky. These costs were reviewed, discussed and reported in previous reports. Changing economic conditions will affect the cost of steel and will require review of these construction costs in the future.

ORNL has completed the tensile testing matrix at three different pressures (800, 1,600, 3,000 psi) and two different strain rates (10^{-4}, 10^{-5}) for the four commercially selected pipeline steels (Alloys A-D) in Table 1 (grade, base chemistry, microstructural characterization comparisons) [1]. The results were reported in previous reports; however Figure 1 shows results from 10^{-5} strain rate for review. From this work, Alloys B and D were chosen for additional fracture and fatigue testing for full mechanical property characterization at 800 and 3,000 psi.

Fracture toughness testing measuring (K_{JIC}) was completed on Alloys B and D at 800 and 3,000 psi (5.5 and 21 MPa) [2]. Both alloys performed well however, Alloy B with the ferrite/coarse acicular ferrite microstructure performed better at each pressure,

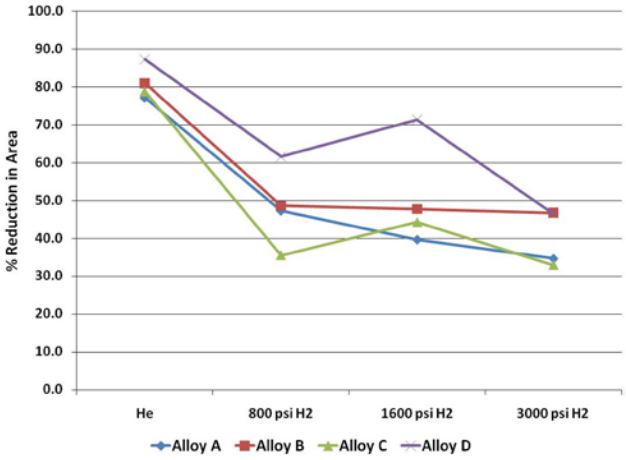

FIGURE 1. In Situ High-Pressure Gaseous Hydrogen Tensile Test Results (Reduction in Area) at 10^{-5} Strain Rate from ORNL of Alloys A – D

TABLE 1. Alloys and Microstructures Tested in Gaseous Hydrogen

	Grade	C	Mn	Si	Cu	Ni	V	Nb	Cr	Microstructure
A	API X70	.08	1.53	.28	.01	0	.05	.061	0.01	92% Polygonal Ferrite/8% Upper Bainite
B	API X70/ X80	.05	1.52	.12	.23	.14	.001	.092	0.25	90% Polygonal Ferrite/10% Coarse Acicular Ferrite
C	API X70/ X80	.04	1.61	.14	.22	.12	.0	.096	0.42	90% Polygonal Ferrite/10% Coarse Acicular Ferrite – Small Amount Upper Bainite
D	API X52/ X60	.03	1.14	.18	.24	.14	.001	.084	0.16	100% Polygonal Ferrite
E	100 KSI Yield Structural	.08	1.71	.22	.06	.67	.002	.044	0.01	TBD
F	400 BHN Abrasion Resistant	.15	1.42	.42	.05	.02	.003	.014	0.22	TBD

TBD - to be determined

Figure 2. In addition, opposite to what others have reported, increasing strength did not degrade fracture toughness which demonstrates the importance of microstructures in this pressure range, Figure 3.

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) was completed on Alloys B and D at 800 and 3,000 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 stress intensity factor range values (stress state near the tip of the crack caused by remote loading) during fatigue, (ΔK expressed in MPa $m^{1/2}$), Figures 4 and 5.

Remaining work for Fiscal Year (FY) 2010 and FY 2011 includes:

Steels

- Optical, scanning electron microscope (SEM) and transmission electron microscope (TEM) microstructural characterization of alternative Alloys E and F.
- Fracture and fatigue testing of alternative Alloys E and F at 3,000 psi.
- Publish final report of microstructure vs. mechanical property performance in gaseous hydrogen under pressure for the alloys selected.

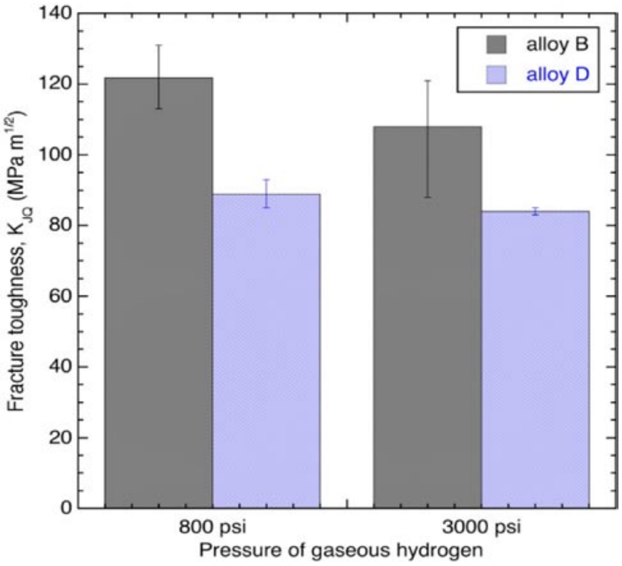

FIGURE 2. Fracture Toughness Results in Hydrogen of Alloys B and D at 800 and 3,000 psi

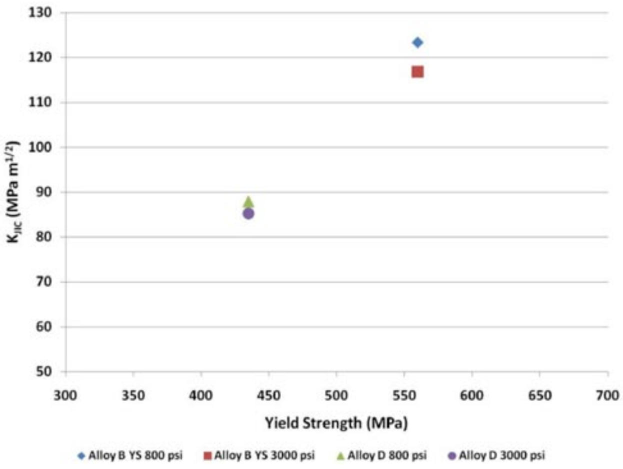

FIGURE 3. Fracture Toughness Results of Alloys B and D vs. Yield Strength

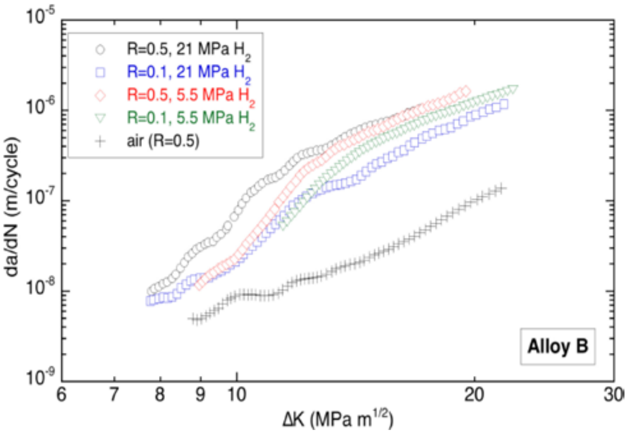

FIGURE 4. Measured Fatigue Crack Growth Rate in Hydrogen (800 and 3,000 psi) and Air of Alloy B at Two R-values

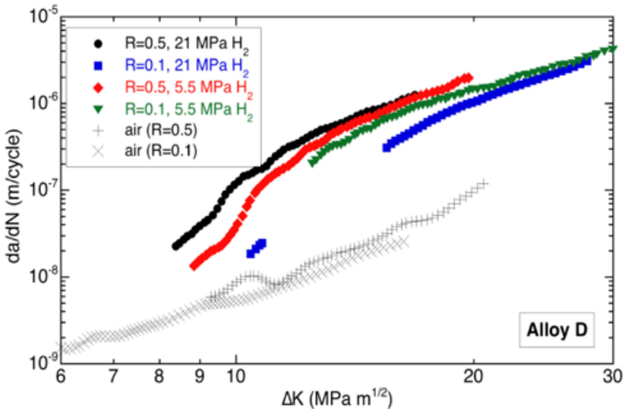

FIGURE 5. Measured Fatigue Crack Growth Rate in Hydrogen (800 and 3,000 psi) and Air of Alloy D at Two R-values

Conclusions and Future Directions

Preliminary testing in FY 2006, FY 2007 and FY 2008 showed that high-pressure hydrogen may have an effect on mechanical properties depending on microstructure design. Additional limited testing at ATC showed that mechanical properties, especially fracture toughness can be affected in the presence of high-pressure hydrogen. NACE testing demonstrated that microstructures, especially those containing pearlite/upper bainite, are susceptible to cracking in the presence of hydrogen. FY 2009 testing at ORNL utilizing high pressure in situ tensile testing confirmed that microstructure does appear to play a role in resistance to the effects of hydrogen, especially with increasing pressure. In FY 2010 testing, fracture toughness testing of the polygonal ferrite microstructure (Alloy D) vs. a polygonal ferrite/10% coarse acicular ferrite microstructure (Alloy B) showed that the acicular ferrite microstructure performed better at both lower and higher hydrogen pressures. There was no significant difference between the Alloy B and Alloy D in fatigue testing, even under two different R-ratio values. There does appear to be a convergence of performance of the two alloys with that tested in air at lower ΔK values. This may be a positive in fatigue performance in relationship to gaseous hydrogen transmission as lower ΔK values may be more realistic in actual operation.

Based on current available funding, the following represents additional work in FY 2010 and FY 2011:

Steels

- Fracture and fatigue testing of Alloys E and F at 3,000 psi gaseous hydrogen.
- Complete microstructural characterization of Alloys E and F by optical microscopy, SEM and TEM evaluation.
- 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 for implementation.
- Evaluate economic impact of suggested materials systems.

Results from the testing will be used to help identify optimum alloy/microstructure design required to safely transport high-pressure hydrogen gas through steel pipelines. Some of these alloy/microstructure designs may already exist in the existing pipeline infrastructure. This work has generated ASME Codes and Standards interest along with private industry that has resulted in additional fracture and fatigue testing to take place of additional alloys/microstructures in a Phase 2 project.

FY 2010 Publications/Presentations

1. An oral presentation regarding the overall project status was given at the DOE Pipeline Working Group Meeting – NIST Boulder, CO (August 2009).

2. Poster presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (June 2010).

3. C. San Marchi, D. Stalheim, T. Boggess, S. Jansto, B. Somerday, G. Muralidharan, and P. Sofronis, "Microstructure and Mechanical Property Performance of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen", ASME 8th International Pipeline Conference, Calgary Alberta, Canada, September 2010.

4. C. San Marchi, D. Stalheim, T. Boggess, S. Jansto, B. Somerday, and K. Nibur, "Fracture and Fatigue of Commercial Grade API Pipeline Steels in Gaseous Hydrogen", ASME Pressure Vessel and Piping Conference, Bellevue, WA, USA, July 2010.

References

1. "Materials Solutions for Hydrogen Delivery" in Pipelines 2010 Poster Presentation from the DOE Annual Merit Review Meeting (June 2010).

2. "C. San Marchi, D. Stalheim, T. Boggess, S. Jansto, B. Somerday, G. Muralidharan, and P. Sofronis, "Microstructure and Mechanical Property Performance of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen", ASME 8th International Pipeline Conference, Calgary Alberta, Canada, September 2010.