III.18 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 Technology 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 2010

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.

- 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.
- Understand the economics of implementing new technologies.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure 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 2012 hydrogen delivery pipeline transmission targets:

- Reliability (relative to hydrogen embrittlement concerns and integrity):
  - Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure 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): $0.60 for 16" outside diameter (OD) 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.

- Majority of the baseline pipeline steel microstructure and mechanical property data have been characterized.
- Commercial X70 pipeline welds available.
- Two traditional screening tests have been explored.
- In situ automated ball indentation 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:
  - 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
- 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 Technology, LLC, 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, ATC 2,000 psi testing, and corrosive National Association of Corrosion Engineers (NACE) testing 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. Reduction in area was measured for each pressure/alloy. All four of the alloy designs had an initial drop in reduction in area at 800 psi hydrogen for each strain rate. However, the drop in reduction in area varied by alloy design (i.e. – microstructure) and with increasing pressure each alloy design performed differently. From this testing the ferrite/acicular ferrite microstructure design of alloys B and D performed the best across the pressure range (Figures 1 and 2). In addition, ORNL performed statistical tensile testing of alloys A and B

TABLE 1. Compositions of Steels Selected for Initial Study of Hydrogen Embrittlement under High Pressure Hydrogen (all in wt%)

	Grade	C	Mn	Si	Cu	Ni	V	Nb	Al	Cr	Ti
A	API X70	0.08	1.53	0.28	0.01	0	0.05	0.061	0.031	0.01	0.014
B	API X70/ X80	0.05	1.52	0.12	0.23	0.14	0.001	0.092	0.036	0.25	0.012
C	API X70/ X80	0.04	1.61	0.14	0.22	0.12	0.0	0.096	0.037	0.42	0.015
D	API X52/ X60	0.03	1.14	0.18	0.24	0.14	0.001	0.084	0.034	0.16	0.014
E*	100 KSI Yield Structural	0.08	1.71	0.22	0.06	0.67	0.002	0.044	0.039	0.01	0.038
F*	400 BHN Abrasion Resistant	0.15	1.42	0.42	0.05	0.02	0.003	0.014	0.038	0.22	0.035

*Alloy E and F contain 0.0017 and 0.0023 boron, respectively. Alloy F contains molybdenum of 0.32.

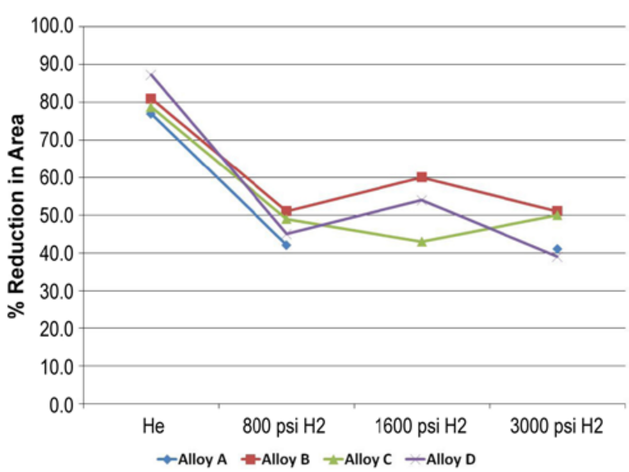

FIGURE 1. In Situ High Pressure Gaseous Hydrogen Tensile Test Results (Reduction in Area) at 10^{-4} Strain Rate from ORNL of Alloys A-D

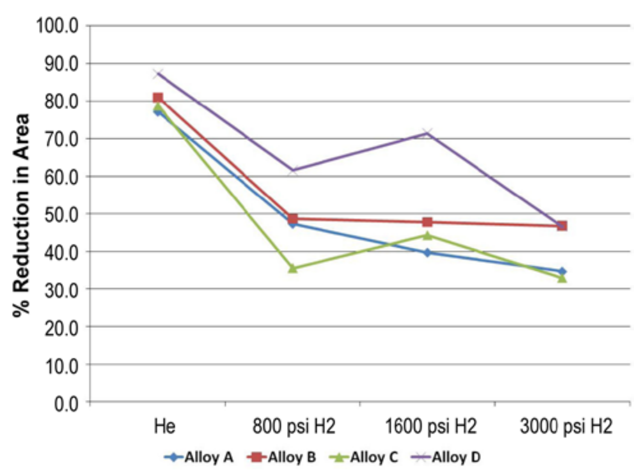

FIGURE 2. In Situ High Pressure Gaseous Hydrogen Tensile Test Results (Reduction in Area) at 10^{-5} Strain Rate from ORNL of Alloys A-D

which in both cases showed no effect on actual yield and ultimate strengths at the three pressure ranges. Fracture stress was the only variable affected in the presence of hydrogen gas (Figures 3 and 4).

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.

Remaining work for Fiscal Year 2009 includes:

- Validation testing of initial ORNL tensile testing of selected data points.
- Transmission electron microscopy microstructural characterization of bainitic structures of alloys A–D.

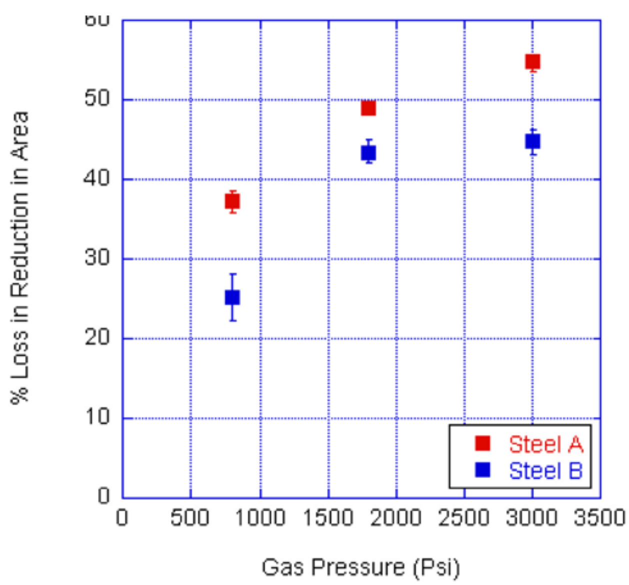

FIGURE 3. In situ High Pressure Gaseous Hydrogen Statistical Tensile Test Results (Reduction in Area) at 10^{-5} Strain Rate from ORNL of Alloys A and B

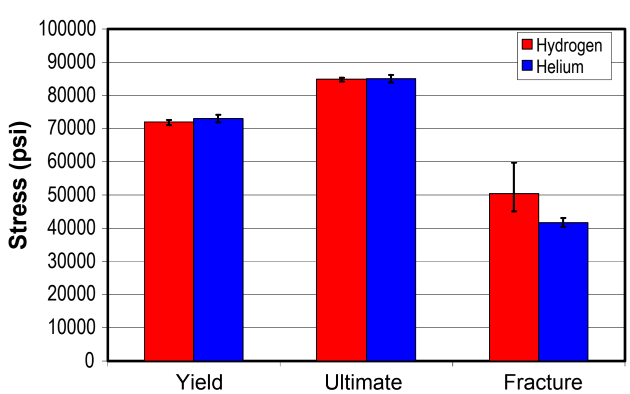

FIGURE 4. In situ High Pressure Gaseous Hydrogen Statistical Tensile Test Results (Strength) at 10^{-5} Strain Rate from ORNL of Alloy B

- Fracture and fatigue testing of alloys B and D at 800 and 3,000 psi.

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 microstructure; especially those containing pearlite are susceptible to cracking in the presence of hydrogen. ORNL high pressure in situ tensile testing has been completed at three different pressures and two strain rates. Using reduction in area as the comparison criteria, two alloys (B and D) had the best performance across the pressure range. This supports that microstructure is a critical component of resistance to hydrogen embrittlement and needs to be fully understood. Alloys B and D were selected for additional fracture and fatigue mechanical testing to complete the mechanical property characterization in the presence of high pressure (800 and 3,000 psi) gaseous hydrogen.

Pending future funding in FY 2010, the following represents additional work:

Steels

- In situ tensile testing of down selected alternative alloy/microstructure (alloy E and F) designs at three pressures (800, 1,600, 3,000 psi) and strain rates (10^{-4}, 10^{-5}).
- Fracture and fatigue testing of best performer of alloys E and F at 800 and 3,000 psi.
- Characterize the effect of one impurity gas on properties evaluated using in situ tensile testing.
- Volume fractions of microstructure thresholds, pressure thresholds, other factors (industrial surface oxide, etc.).
- Complete microstructural characterization of down-selected steels after exposure to hydrogen to understand the effect of microstructure on embrittlement.
- Add alloys with higher volume fraction of pearlite (~10-30%, represents older 1950-1980's pipeline metallurgy) or various volume fractions of bainite or different types of bainite to the in situ testing to evaluate volume fraction thresholds.
- Complete thermodynamic and kinetic modeling of initial down-selected alloys D-F composition.
- Pipeline weld sample microstructural and hydrogen pressure and time can be included in the testing.
- 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.

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.

FY 2009 Publications/Presentations

1. An oral presentation regarding the overall project status was given at the DOE Pipeline Working Group Meeting – Jackson Hole, WY (September 2008).

2. An oral presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2009).

3. G. Muralidharan, J.P. Strizak, N.D. Evans, D.G. Stalheim, and S.K. Das, "Effect of Microstructure on Hydrogen Embrittlement of Pipeline Steels", Hydrogen08 Conference, Jackson Hole, WY USA, 2008.

4. D. Stalheim, L. Hayden, "Metallurgical Considerations for Commercial Steels used for Hydrogen Service", Hydrogen08 Conference, Jackson Hole, WY USA, 2008.

References

1. "Materials Solutions for Hydrogen Delivery" in Pipelines 2008 Oral Presentation from the DOE Pipeline Working Group Meeting, Jackson Hole, WY (September 2008).

2. "Materials Solutions for Hydrogen Delivery" in Pipelines 2009 Oral Presentation from the DOE Annual Merit Review Meeting (May 2009).