III.4 Materials Solutions for Hydrogen Delivery in Pipelines

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Subcontractors:

- 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

Start Date: May 2005
Projected End Date: September 2009

Objectives

The 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.

- To identify steel compositions and associated welding filler wires and processes that would be suitable for construction of new pipeline infrastructure or indicate use of an existing pipeline infrastructure.
- To develop barrier coatings for minimizing hydrogen permeation in pipelines and to develop in situ deposition processes suitable for these coatings.
- 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.

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 2010 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.
  - Evaluate the hydrogen embrittlement in alloys coated with selected coatings.
- Pipeline Transmission Total Capital Cost ($M/Mile): $0.80
  - 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.

- Microstructural work, mechanical property testing, continuous cooling transformation curves computationally generated, ex situ high pressure hydrogen testing, ATC stress strain microprobe high pressure hydrogen testing, National Association of Corrosion Engineers (NACE) testing, thermal expansion characterization of glass coating compatibility (on hold per DOE) of several of the selected pipeline alloys has been completed.
- Oak Ridge National Laboratory (ORNL) has completed construction of specialized device for tensile testing in the presence of high pressure hydrogen gas with the ability to vary strain rates during testing.
- Actual construction costs of a pipeline project supplied by Columbia Gas of Kentucky reviewed by the project team.
- ORNL has started tensile testing in the presences of high pressure hydrogen gas of Alloy "A" and Alloy "C".

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., American Society of Mechanical Engineers (ASME), University of Illinois, Schott North America-Regional R&D, Columbia Gas, Chemical Composite Coatings International LLC, Advanced Technology Corporation, Oregon Steel Mills, 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

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.

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 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. The current rapidly escalating cost of steel will require review of these construction costs in the future.

The equipment for mechanical testing in situ in a hydrogen atmosphere at high pressures at ORNL has been completed this year. Tensile testing has begun on Alloys A and B. Testing has been done at 1,580 psi in the presence of hydrogen and helium for comparison. In addition, due to the equipment's capability to vary strain rate and this parameter as being cited as something to be evaluated, testing has begun in varying strain rate. Preliminary results show that the presence of hydrogen has an effect. However, there appears to be some difference in the behavior between the two microstructures that needs to be further evaluated, see Figures 1-4. The question remains is if this effect is detrimental to the performance of the pipeline. There is still much work to be done in this analysis.

Remaining work for Fiscal Year 2008 includes:

- A tensile testing matrix has been developed for commercial pipeline steel Alloys A-D
  - Three different test pressures (800 psi, 1,600 psi, 3,000 psi)
  - Two different strain rates (10^{-4}, 10^{-5})
  - Two different gas mediums (hydrogen, helium)

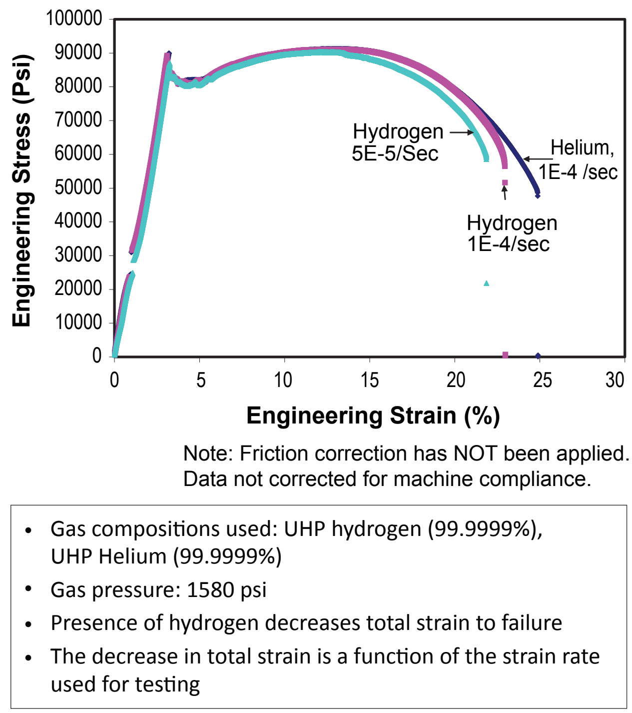


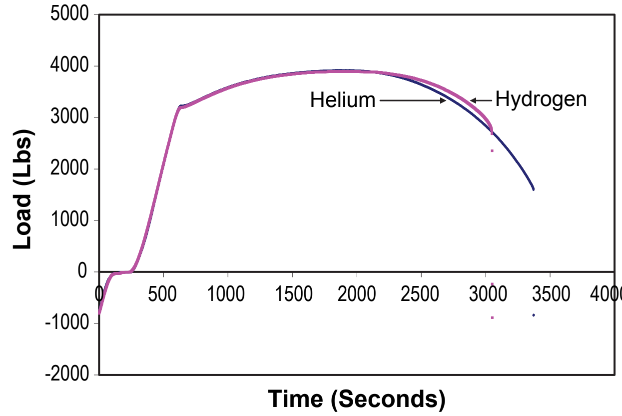
FIGURE 1. In Situ Test Results at 1,580 psi from ORNL of Alloy A in Hydrogen and Helium

- Evaluate effect of different strain rates for in situ testing

Conclusions and Future Directions

Preliminary testing in FY 2006 and FY 2007 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. The ORNL high pressure in situ tensile testing device has been completed. Preliminary in situ testing at ORNL continues to show that microstructural behavior

FIGURE 2. In Situ Test Results at 1,580 psi from ORNL of Alloy A in Hydrogen and Helium, Fracture Mode Changes



- Gas compositions used: UHP hydrogen (99.9999%), UHP Helium (99.9999%)
- Gas pressure: 1580 psi strain rate 10^{-4}
- Presence of hydrogen decreases total strain to failure

FIGURE 3. In Situ Test Results at 1,580 psi from ORNL of Alloy C in Hydrogen and Helium

in the presence of hydrogen can vary. All of this supports that microstructure is a critical component of resistance to hydrogen embrittlement and needs to be fully understood. Additional in situ testing varying pressures and strain rate will be carried out at ORNL on commercial pipeline Alloys A-D. Actual material costs on a recently completed natural gas pipeline projects was 17% of the total construction cost, however will have to be re-evaluated with the dynamic changes in world steel pricing. Initial glass coatings have been selected and methods are being explored to properly coat the permeation samples for the University of Illinois to measure the effectiveness of the glass coatings to hinder hydrogen migration.

Pending future funding in FY 2009, the following represents additional work:

- Steels
  - Complete microstructural characterization of down-selected steels before and after exposure to hydrogen to understand the effect of microstructure on embrittlement.
  - Evaluate in situ fatigue testing of commercial pipeline steels and alternative microstructures.
  - Perform and evaluate baseline fracture mechanics characteristics.
  - Complete thermodynamic and kinetic modeling of initial down-selected steels D-F compositions.
  - Complete microstructural characterization of down-selected steels before and after exposure to hydrogen to understand the effect of microstructure on embrittlement.
  - Start testing and evaluation of other selected Alloys E and F in presence of hydrogen.
  - Pipeline weld sample microstructural and hydrogen pressure and time can be included in the testing.
- Economic Analysis
  - Recommend steel and coating systems for implementation.
  - Evaluate economic impact of suggested materials system.
  - Continued analysis into cost factors (escalating steel prices, etc.) will be require evaluation of options for lowering material and construction costs.

Helium
Typical Ductile cup and cone fracture

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

FIGURE 4. In Situ Test Results at 1,580 psi from ORNL of Alloy C in Hydrogen and Helium, Fracture Mode Changes

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.

FY 2008 Publications/Presentations

1. An oral presentation regarding the overall project status was given at the DOE Pipeline Working Group Meeting - Sandia National Laboratory (February 2008).

2. An oral presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (June 2008).

References

1. "Materials Solutions for Hydrogen Delivery" in Pipelines 2007 Poster Presentation from the DOE Annual Merit Review Meeting (May 2007).

2. "Materials Solutions for Hydrogen Delivery" in Pipelines 2008 Oral Presentation from the DOE Annual Merit Review Meeting (June 2008).

3. "Materials Solutions for Hydrogen Delivery" in Pipelines 2008 Oral Presentation from the DOE Pipeline Working Group Meeting - Sandia National Laboratory (February 2008).