III.A.3 Materials Solutions for Hydrogen Delivery in Pipelines

Subodh Das
Secat, Inc.
Coldstream Research Campus
1505 Bull Lea Rd.
Lexington, KY 40511
Phone: (859) 514-4989; Fax: (859) 514-4988
E-mail: skdas@engr.uky.edu

DOE Technology Development Manager:
Mark Paster
Phone: (202) 586-2821; Fax: (202) 586-9811
E-mail: Mark.Paster@ee.doe.gov

DOE Project Officer: Jill Gruber
Phone: (303) 275-4961; Fax: (303) 275-4753
E-mail: Jill.Gruber@go.doe.gov

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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, 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

Start Date: May 2005
Projected End Date: April 2008

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
  - To identify steel compositions and associated welding filler wires and processes that would be suitable for construction of new 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 (3.2.4.2) 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

(J) Safety, Codes and Standards, Permitting and Sensors

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 H2 embrittlement concerns and integrity) – understood
  - Evaluate hydrogen embrittlement characteristics of existing commercial pipeline 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): $1.00
  - Financial Analysis and Incorporation into Codes and Standards

Accomplishments

Work has been severely curtailed due to limited funding in FY 2006. Accomplishments to date are as follows:

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

- Microstructural work started along with continuous cooling transformation (CCT) curves computationally generated for three of four selected alloys.
- Effect of high pressure hydrogen exposure on three steels has been studied using *ex-situ* tests.
- ORNL started work on the high pressure hydrogen testing device.
- Advanced Technology Corporation (ATC) completed stress strain microprobe (SSM) testing on four alloys and non-destructively measured their tensile and fracture toughness properties in the as-received condition.
- ATC started working on a 5,000 psi hydrogen pressure chamber for *in-situ* SSM testing of uncoated and coated pipeline steel samples.
- Thermal expansion characterized on two steel alloys for glass coating compatibility. Initial glass coatings identified for testing in hydrogen atmosphere.
- Task list revamped to reflect FY 2006 funding shortfalls.

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. Literature currently available clearly shows that hydrogen embrittlement of pipeline steels is one of the limiting factors in the cost-effective, high-pressure transport of hydrogen. 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) development of barrier thin film coatings that would minimize the hydrogen permeation in the current natural gas pipelines, (2) identification of steel compositions and associated welding filler wires and processes that would be suitable for new pipeline infrastructure for transport of hydrogen at requisite high pressures, 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, 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 (see Table 1). 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.

TABLE 1. Vintage, Commercial, and Alternative Grade Pipeline Steels for Evaluation

Grade	Code	C	Source	Comment
Vintage	?	0.30	ORNL 2	Rep. Older Line
Vintage	?	0.18	ORNL 2	Rep. Older Line
X70 Std	A	0.08	OSM	Current Std
X70/X80	B	0.05	OSM	Potential
X70/X80	C	0.04	OSM	Potential
X52/X60 HIC	D	0.03	OSM	Consider Best
Bainitic/Mart	E	0.10	OSM	Optional Micro
Martensite	F	0.14	OSM	Optional Micro

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 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 2. All compositions represent steels that are microalloyed. Steel A represents chemistry used in pipelines in the past 10-15 years, B and C represents chemistries used recently in pipelines while Steel D represents a sour service grade. 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.

These alloys have already been received from our industrial partner Oregon Steel Mills. Thermokinetic modeling and microstructural characterization of three of the steels were completed and reported last quarter. In addition to microstructural characterization, samples have been machined for mechanical testing. Tensile specimens conforming to ASTM-E8 have been machined from three alloys, A, B, and C. Initial tensile tests have been conducted at ORNL to survey the mechanical properties of these steels, which will serve as a baseline assessment. In addition, mechanical properties were measured on all four selected alloys using the Automated Ball Indentation (ABI) testing method to be used as reference for *in situ* high pressure hydrogen testing (see Table 3).

Samples were sent to Dr. Brian Somerday at Sandia National Laboratory, Livermore for a preliminary study of embrittlement using *ex-situ* high-pressure hydrogen charging, and tensile testing. Samples were charged under 20,000 psi hydrogen at 100°C for 8 days. To account for any temperature effects, another set of specimens was tested after exposure to 5,000 psi helium at 100°C for 8 days.

TABLE 2. Compositions of Steels Selected for Initial Study of Hydrogen Embrittlement under High Pressure Hydrogen (all in wt%)

	API Grade	C	Mn	Si	Cu	Ni	V	Nb	Al	Cr	Ti
A	X70	0.08	1.53	0.28	0.01	0.00	0.050	0.061	0.031	0.01	0.014
B	X70/ X80	0.05	1.52	0.12	0.23	0.14	0.001	0.092	0.036	0.25	0.012
C	X70/ X80	0.04	1.61	0.14	0.22	0.12	0.000	0.096	0.037	0.42	0.015
D	X52/X60	0.03	1.14	0.18	0.24	0.14	0.001	0.084	0.034	0.16	0.014

TABLE 3. ABI Measured Baseline Mechanical Properties of Four Selected Alloys

Sample ID All API Plate Samples	YS	Calc. Eng. UTS	Calc. Unif. Ductility	YS/UTS Ratio	Hardness ABI-H	Fracture Toughness
	(ksi)	(ksi)	(%)			(ksi*in ^ 0.5)
API X70, A-1	82.8	102.3	7.9	0.81	242	217.8
API X70, A-2	82.3	101.3	7.8	0.81	240	216.2
API X70, A-3	81.4	100.9	8.0	0.81	239	214.4
API X80, B-1	74.9	93.4	8.1	0.80	220	207.0
API X80, B-2	75.0	94.7	8.3	0.79	221	210.4
API X80, B-3	77.4	94.3	7.6	0.82	225	208.5
API X80, C-1	86.4	104.8	7.5	0.82	252	219.4
API X80, C-2	84.8	104.5	7.9	0.81	248	216.3
API X80, C-3	86.2	105.9	7.6	0.81	252	218.9
API X60, D-1	64.6	77.6	7.3	0.83	185	191.6
API X60, D-2	63.9	77.6	7.5	0.82	185	190.7
API X60, D-3	63.8	78.4	8.1	0.81	189	194.5

Figures 1-3 show the results of tensile tests from Steels A, B, and C along with their microstructures. Table 4 shows a summary of the test results. Results show that there is very little effect of hydrogen charging in Steel B but a tendency to reduce the failure strains in Steels A and C. These results are preliminary and need to be studied in greater detail. This is the beginning of numerous high pressure hydrogen testing that needs to be completed to understand the effect of high pressure hydrogen gas on the embrittlement of various pipeline steel alloy/microstructure designs.

Glass coating development has been progressing. Five customized glass compositions have been melted. Precursors for coating processes have been prepared. Identification and pre-evaluation of low-cost approaches to coat the inside of steel tubes (paint-on-burn-in, others) has been explored. Test coating of flat pipeline steel samples to determine process parameters and compatibility of the glass with the steel substrate has been completed. Thin, dense and crack/pit-free coatings have been obtained in a multi-step, modified enamel process. Coatings exhibit good adherence, but can be removed by sandblasting.

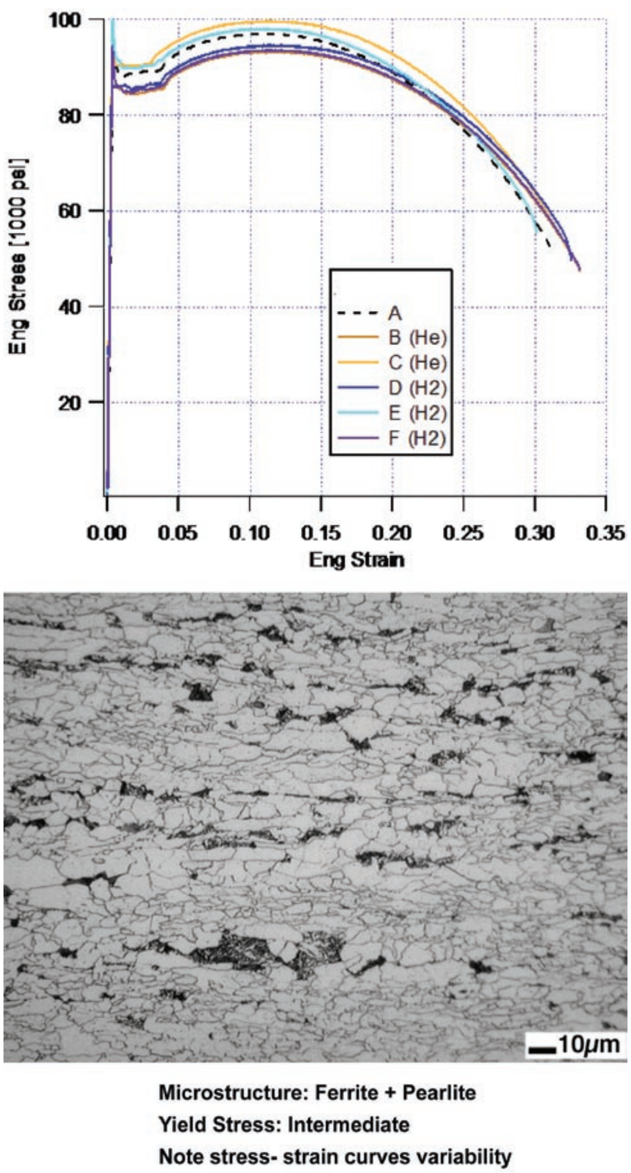

FIGURE 1. Stress-Strain Curves and Microstructure from Specimens of Steel A after *Ex-Situ* Hydrogen Charging under High Pressures

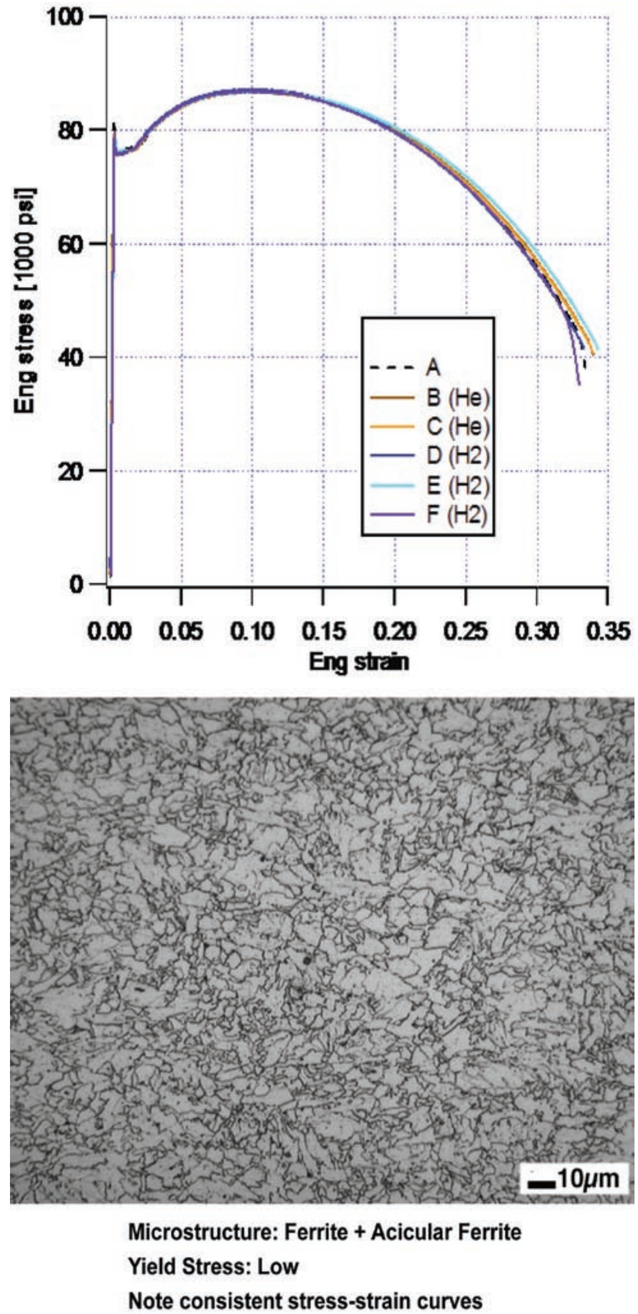

FIGURE 2. Stress-Strain Curves and Microstructure from Specimens of Steel B after *Ex-Situ* Hydrogen Charging under High Pressures

Significant progress has also been achieved in the assembly of equipment for mechanical testing *in-situ* in a hydrogen atmosphere at high pressures at both ORNL and ATC. An internal safety review has been performed and approval for proceeding with assembly of the facility has been granted. A detailed safety plan was completed and provided to DOE. Figures 4 and 5 show the various assembled pieces of equipment for mechanical testing of steels in high pressure hydrogen atmospheres at both ORNL and ATC.

Remaining work for FY 2006 included volume fraction microstructural analysis of the four selected alloys along with 2000 psi hydrogen testing of alloys A and D in both an un-coated and glass coated condition at ATC. In addition, pipeline steel samples from an outside source will be included in the ATC hydrogen testing for comparison. Samples of pipeline welds have been secured and will be used in future work.

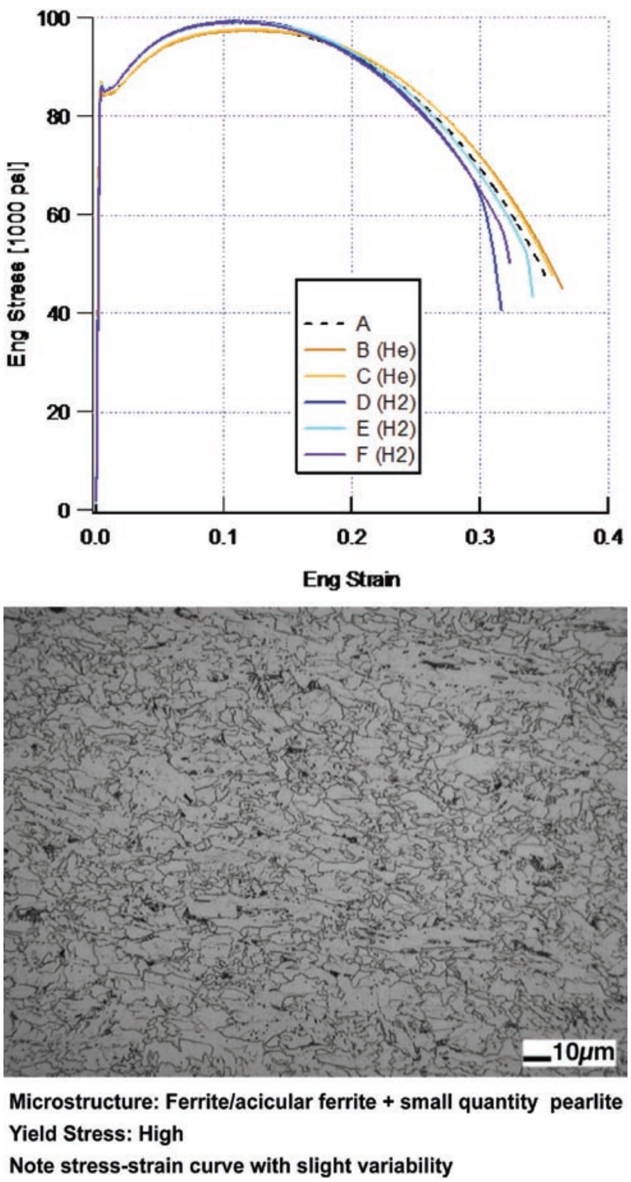

FIGURE 3. Stress-Strain Curves and Microstructure from Specimens of Steel C after *Ex-Situ* Hydrogen Charging under High Pressures

TABLE 4. Ex-Situ High Pressure Hydrogen Mechanical Testing Summary of Steels A, B, and C

Material		ID	Note	Min Diameter [in]	Failure Strain	Tensile Modulus [10^6 psi]	
X70	A	A	As is	0.1605	0.31	26.6	Medium YS
		B	He	0.1605	0.33	29.2	
		C	He	0.1612	0.32	31.9	
		D	H_2	0.1608	0.32	31.4	
		E	H_2	0.1607	0.30	29.5	
		F	H_2	0.1605	0.33	28.7	
X80	B	A	As is	0.1601	0.33	30.5	Low YS
		B	He	0.1605	0.34	33.8	
		C	He	0.1603	0.34	32.7	
		D	H_2	0.1603	0.33	29.8	
		E	H_2	0.1606	0.34	29.9	
		F	H_2	0.1605	0.33	29.6	
X80	C	A	As is	0.1609	0.35	28.9	High YS
		B	He	0.1607	0.36	31.3	
		C	He	0.1602	0.36	30.4	
		D	H_2	0.1601	0.32	28.0	
		E	H_2	0.1602	0.34	29.5	
		F	H_2	0.1603	0.32	29.8	

Conclusions and Future Directions

Due to curtailed funding, major work on this project was ceased at the direction of the DOE. Preliminary testing shows that high pressure hydrogen may have an effect on mechanical properties depending on microstructure design. High pressure hydrogen testing equipment is completed or close to completion at both ORNL and ATC. Initial glass coatings have been developed that are compatible with the selected pipeline steels. Limited high pressure hydrogen testing will be completed in FY 2006 by ATC.

Pending future funding in FY 2007, completion of the ORNL high pressure hydrogen testing unit can be accomplished. Additional testing of other alloy/microstructure designs at both ATC and ORNL in the presence of hydrogen gas over various pressures and times to evaluate hydrogen embrittlement mechanisms can be completed. Permeation studies of the un-coated

FIGURE 4. Various Critical Components and Partially Assembled Systems that will be utilized for Delivery of High-Pressure Hydrogen to the Mechanical Testing System at ORNL

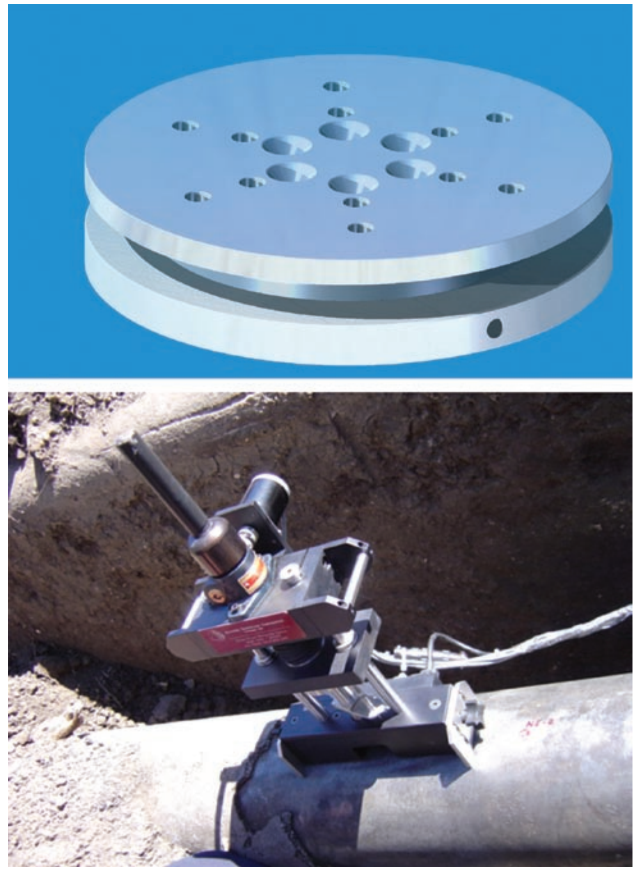

FIGURE 5. ATC SSM Hydrogen Chamber (top) allows conducting five ABI tests on each of six pipeline steel samples (1-inch diameter, 0.375-inch thick) at high hydrogen pressure and at various increasing exposure times using ATC's portable/in-situ SSM system (bottom)

and coated samples will be done. Pipeline weld sample microstructural and hydrogen pressure and time can be included in the testing. Continued analysis into cost factors will be continued to evaluate options for lowering material and construction costs.

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 2006 Publications/Presentations

1. 4th quarter project report prepared December 31, 2005.

2. A poster presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2006).

3. Panel participation Second Panel Forum Hydrogen Pipeline Transmission: Updates and Opportunities, ASME 6th International Pipeline Conference, Calgary, Canada September 2006.

4. Technical publication ASME 6th International Pipeline Conference, Calgary Canada September 2006, "The Role of Continuous Cooling Transformation Diagrams in Material Design for High Strength Oil and Gas Transmission Pipeline Steels."

References

1. "Materials Solutions for Hydrogen Delivery" in Pipelines 2006 Poster Presentation from the DOE Annual Merit Review Meeting (May 2006).

2. "Materials Solutions for Hydrogen Delivery" 4th Quarter Project Report.

3. "Materials Solutions for Hydrogen Delivery" Presentation at DOE Hydrogen Workshop, Augusta, GA. (August 2005).