Materials Solutions for Hydrogen Delivery in Pipelines

Dr. Subodh K. Das

Secat, Inc.

May 15, 2007

Project ID: PDP18

Overview

Timeline

- Project start date: 05/2005
- Project end date: 09/2009
- Percent complete: 15%

Budget

- Total project funding
  - $1650K (DOE share)
  - $1110K (contractor share)
- Funding for FY 05: $200K
- Funding for FY 06: $155K
- Funding expected for FY 07: $500K

Barriers and Targets

Barriers addressed

High capital cost and Hydrogen Embrittlement of Pipelines

Technical Targets (2015):

– Capital cost ($0.8 Million/Mile)

– Cost of delivery of hydrogen <$1.00/gge

– High Reliability of operation with metrics to be determined

Partners

SECAT CONSORTIUM

- **Advanced Technology Corporation**
- **ASME Standards and Technologies, LLC**
- **Chemical Composite Coatings Intl**
- **Columbia Gas of Kentucky**
- **Oregon Steel Mills**
- **Schott North America**
- **DGS Metallurgical Solutions, Inc.**
- **Hatch Moss MacDonald**

Oak Ridge National Laboratory

University of Illinois

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 overall objectives of the project are:**
  - **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**

Objectives

FY05	– Kick off meeting – Internal milestones for individual project team-members were defined. – Commercially available pipeline steels identified for study. – Mechanical properties/microstructures characterization started.
FY06 (limited funding)	– Begin construction of high pressure testing equipment (ORNL,ATC) – Initial high pressure testing at 2000 psi for 200 hours completed on Alloy A an D at ATC. – Develop suitable coatings. – Detailed microstructural characterization completed.
FY07 (delayed funding)	– Conducted NACE HIC Solution A testing of four selected alloys A, B, C, and D. – Begin glass coating by Schott NA of machined samples for permeation testing at University of Illinois. – Finish construction of high pressure testing equipment at ORNL and being testing. – Conduct permeation testing at the University of Illinois of un-coated and coated machined samples from the four selected alloys. – Reviewed actual costs to construct steel pipeline as supplied by Columbia Gas of Kentucky. – Restart cost model through ORNL.

Key Technical Barriers

- Extent of hydrogen embrittlement of base material, and welds in pipeline steels and other common steels on exposure to high pressure H_2 is not known
- Only a limited understanding of the mechanisms of hydrogen embrittlement along with the effect of metallurgical variables such as alloying element additions, and microstructure of steels is available at the present time; hence the path to remediation and control is not well defined
- Although it is known that barrier coatings are effective in reducing hydrogen embrittlement, detailed knowledge of the effectiveness of various metallic and non-metallic coatings in minimizing the deleterious effect of H_2 under high pressures is not known
- Very little information is available on the potential avenues for reducing the cost of construction of pipelines for transport of hydrogen and the cost of technologies to remediate the effect of hydrogen embrittlement

Approach

Task 1: Evaluate high-pressure hydrogen embrittlement characteristics (15% Comp.)

- Select commercial grade pipeline steels for study
- Characterize steels
- Build testing equipment
- Test and evaluate steels

Task 2: Develop and/or identify alternate alloys (5% Comp.)

- Identify alternate alloy and microstructures in steels including Task 1 data
- Computational thermodynamic and kinetic modeling techniques
- New alloy compositions will be identified and small heats of alloys will be prepared
- Hydrogen embrittlement characteristics evaluated, refinement of alloy design based on results

Task 3: Develop coatings to minimize dissolution and penetration of hydrogen (15% Comp.)

- Coatings from two industrial partners: multi-component oxides with rare earths and glass coatings
- Coating chemistries and processes developed
- Quality and characterization of coatings will be evaluated
- Chemistries of coatings, and deposition processes optimized for Task 4

Task 4: Evaluate the hydrogen embrittlement in alloys coated with selected coatings (0% Comp.)

- Short-term effect of coatings on hydrogen embrittlement will be evaluated using *in-situ* mechanical testing in high pressure hydrogen
- Long-term effectiveness in minimizing hydrogen embrittlement characterized Automated Ball Indentation tests on pipes, and welds
- Microstructural characterization will be carried out to study the effect of coatings on failure mechanisms
- Effect of procedures such as pigging on coating effectiveness will also be evaluated
- Promising coating-substrate combinations will be identified for further development and cost analysis

Task 5: Perform financial analyses and incorporate knowledge into codes and standards (10% Comp.)

- The cost of a typical pipeline installation includes many cost components
- ORNL and industry partners will develop a financial analysis model-FLOW
- On-going cost analysis updating as new information is available
- Coordination with DOE H2A analysis
- Use output to re-focus project if and as appropriate vs. the goal, objectives, and targets for the DOE Hydrogen Program

Technical Accomplishments/ Progress/Results

- Hydrogen embrittlement of steels has been characterized using cathodically charged specimens in the literature

- Very little data is available on the effect of high pressure hydrogen on the embrittlement of various line pipe steels

- One of the important objectives of the project is:
  - To develop information on the effect of
    - steel composition, and
    - steel microstructure

  on the hydrogen embrittlement due to exposure to high pressure hydrogen

Technical Accomplishments/ Progress/Results – Commercial Steels for Evaluation

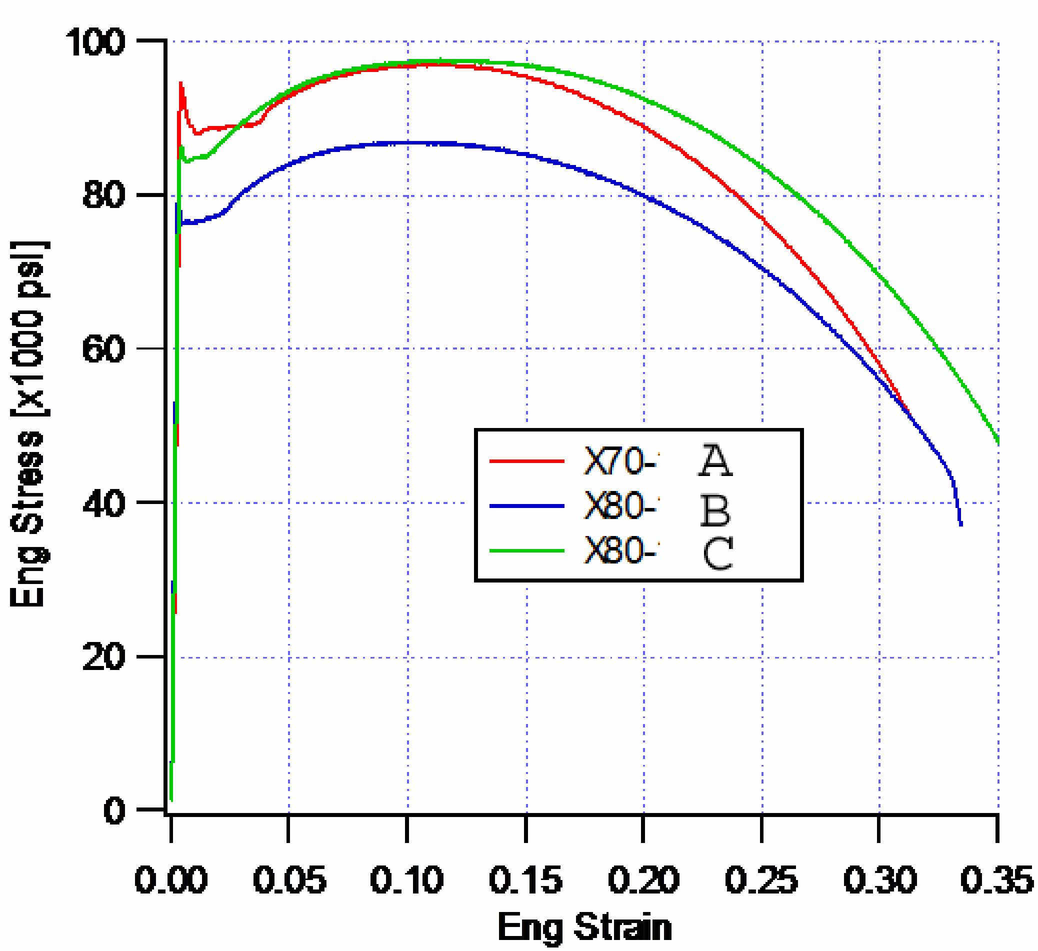
Grade	Code	C	Source	Comment
Vintage	?	0.30	ORNL 2	Rep. Older Line
Vintage	?	0.18	ORNL 2	Rep. Older Line
X70 Std	A	0.08	OSM	Current Std
X70/X80	B	0.05	OSM	Potential
X70/X80	C	0.04	OSM	Potential
X52/X60 HIC	D	0.03	OSM	Consider Best
Bainitic/Mart	E	0.10	OSM	Optional Micro
Martensite	F	0.14	OSM	Optional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

Technical Accomplishments/ Progress/Results – Work Done to Date

- Microstructural work completed along with CCT curves computationally generated for alloy's "A", "B", and "C".
- Effect of high pressure hydrogen exposure on three steels has been studied using *ex-situ* tests
- ORNL started work on high pressure hydrogen testing device.
- ATC completed SSM testing on four alloys ("A", "B", "C", "D") and non-destructively measured their tensile and fracture toughness properties in the as-received condition.
- ATC completed work on a 5000 psi hydrogen pressure chamber for *in-situ* SSM testing of uncoated and coated pipeline steel samples.
- ATC tested uncoated samples of Alloy "A – X70", "D" – X52/X60" along with outside supplied pipeline grades B and X80 for hydrogen gas testing at 2000 psi at a total exposure time of 200h.
- Thermal expansion characterized on two steel alloys for glass coating compatibility. Initial glass coatings identified for testing in hydrogen atmosphere. Glass coating process applied to machined samples for University of Illinois permeation testing.
- NACE HIC Solution A testing completed on four alloys "A", "B", "C", and "D".
- Task list revamped to reflect FY06 funding shortfalls and modified for FY07 based on anticipated funding level.

Technical Accomplishments/Progress/Results - Baseline Properties of Steels Obtained Using ASTM-E8 specimens

(No hydrogen)



Technical Accomplishments/Progress/Results – Summary of ABI Measured Mechanical Properties of Selected Steels

Sample ID All API Plate Samples	YS (ksi)	Calc. Eng. UTS (ksi)	Calc. Unif. Ductility (%)	YS/UTS Ratio
API X70, A-1	82.8	102.3	7.9	0.81
API X70, A-2	82.3	101.3	7.8	0.81
API X70, A-3	81.4	100.9	8.0	0.81
API X80, B-1	74.9	93.4	8.1	0.80
API X80, B-2	75.0	94.7	8.3	0.79
API X80, B-3	77.4	94.3	7.6	0.82
API X80, C-1	86.4	104.8	7.5	0.82
API X80, C-2	84.8	104.5	7.9	0.81
API X80, C-3	86.2	105.9	7.6	0.81

- Yield Strength of B < A < C
- Data is Consistent with traditional tensile tests

Technical Accomplishments/Progress/Results – Microstructural Analysis of Current Pipeline Alloy Designs

- The microstructures of the four selected alloy designs where characterized
  - Alloy A shows a ferrite/pearlite microstructure. The pearlite was banded and varying from 4% at the surface layer to 6 to 8% towards the center by volume.
  - Alloy B shows a ferrite/acicular ferrite microstructure with no change in the grain size from surface to center
  - Alloy C shows a ferrite/acicular ferrite microstructure with no change in the grain size from surface to center
  - Alloy D shows a ferrite/acicular ferrite microstructure with the grain size increasing from the surface to center

Additional work will be needed to further classify the volume fraction of acicular ferrite is present in Alloys B, C, and D

Technical Accomplishments/Progress/Results – NACE HIC Testing of Current Pipeline Alloy Designs

- The four selected current pipeline alloy designs were tested in accordance to NACE TM0284 Solution A for evaluation of the microstructures resistance to hydrogen cracking.
- Literature suggest that pipeline microstructures that are designed to resist hydrogen cracking in a sour service corrosive environment as dictated by NACE TM0284 maybe suitable for use in high pressure hydrogen gas transport.

Technical Accomplishments/Progress/Results – NACE HIC Testing of Current Pipeline Alloy Designs

Alloy	NACE %CLR	NACE %CSR	NACE %CTR
A	11.8	0	0.1
B	0.4	0	0
C	0	0	0
D	0	0	0

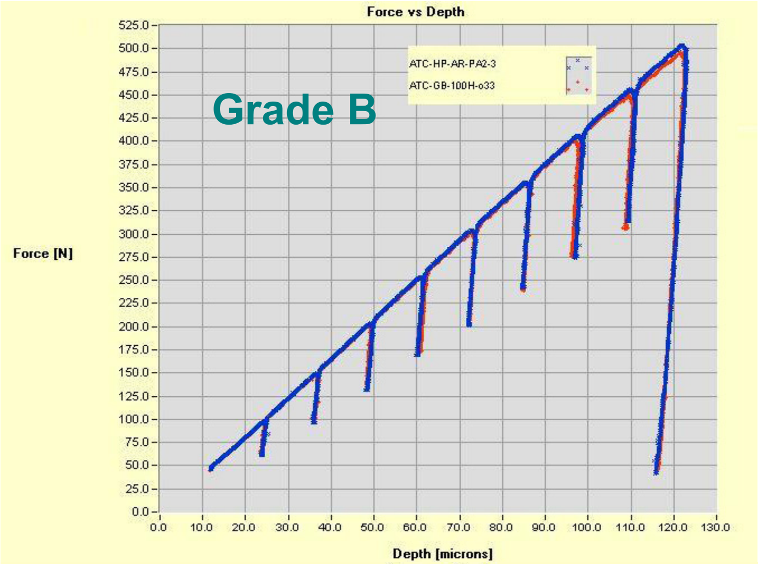
Technical Accomplishments/Progress/Results – Precision Machining of Samples for ATC, Schott North America, University of Illinois

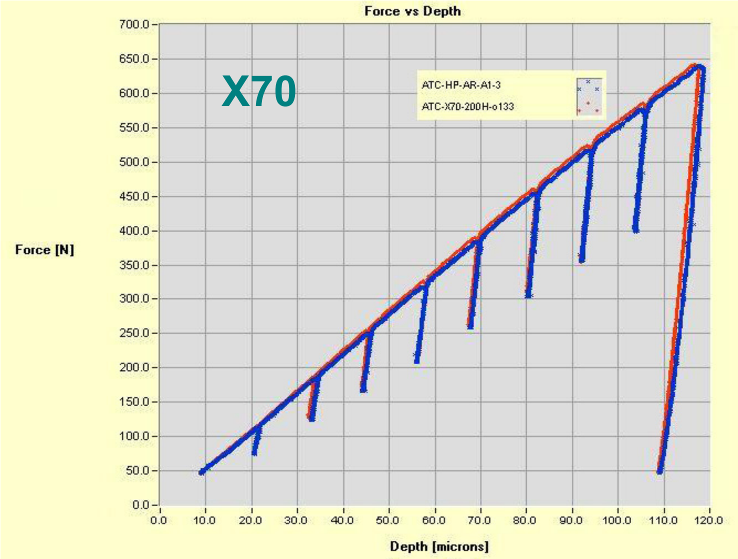
- Samples of four select current pipeline alloy designs have been machined for the following testing:
  - ATC High Pressure testing
  - Permeability testing at University of Illinois
  - Glass coating trials at Schott North America to be used in permeability testing at University of Illinois to test the effectiveness of glass coating on hydrogen permeability under pressure.

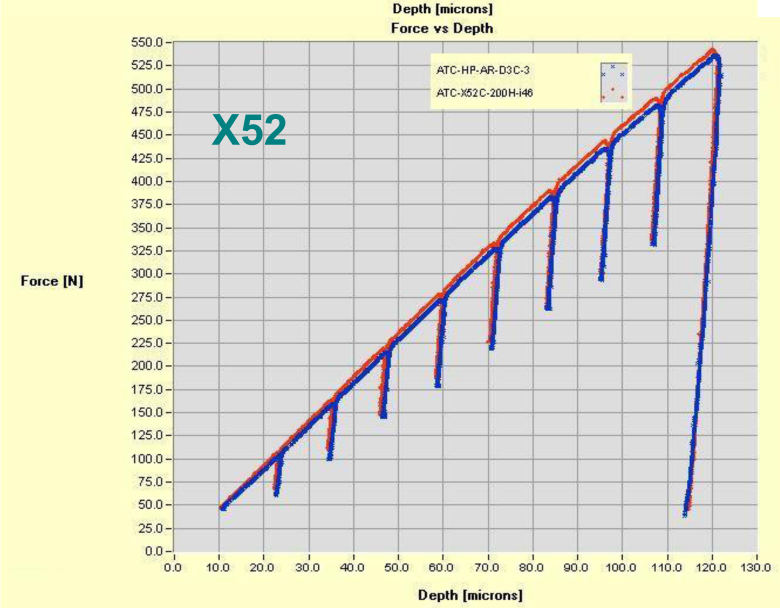
Technical Accomplishments/Progress/Results:

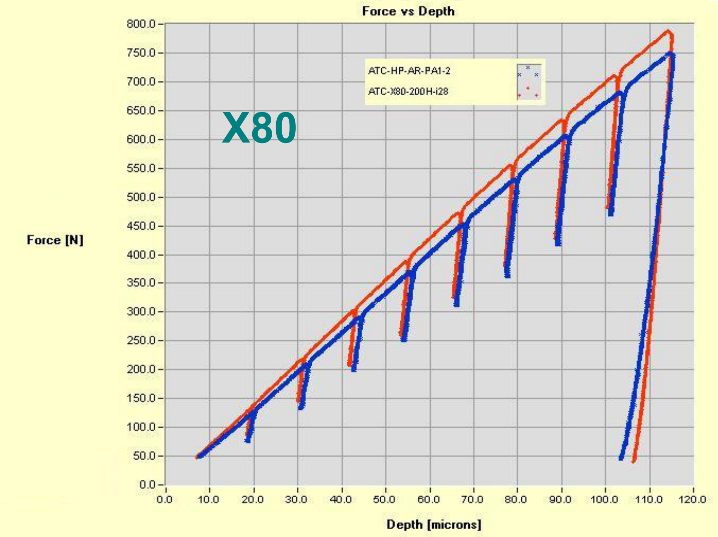
In-Situ SSM Testing System - Hydrogen Chamber allows simultaneous exposure of 6 pipeline steels and performing up to 16 ABI tests on each disc at various times

Technical Accomplishments/Progress/Results:
In-Situ SSM Testing System -Effects of 200 h exposure to 2,000 psi hydrogen on ABI data of four pipeline steels

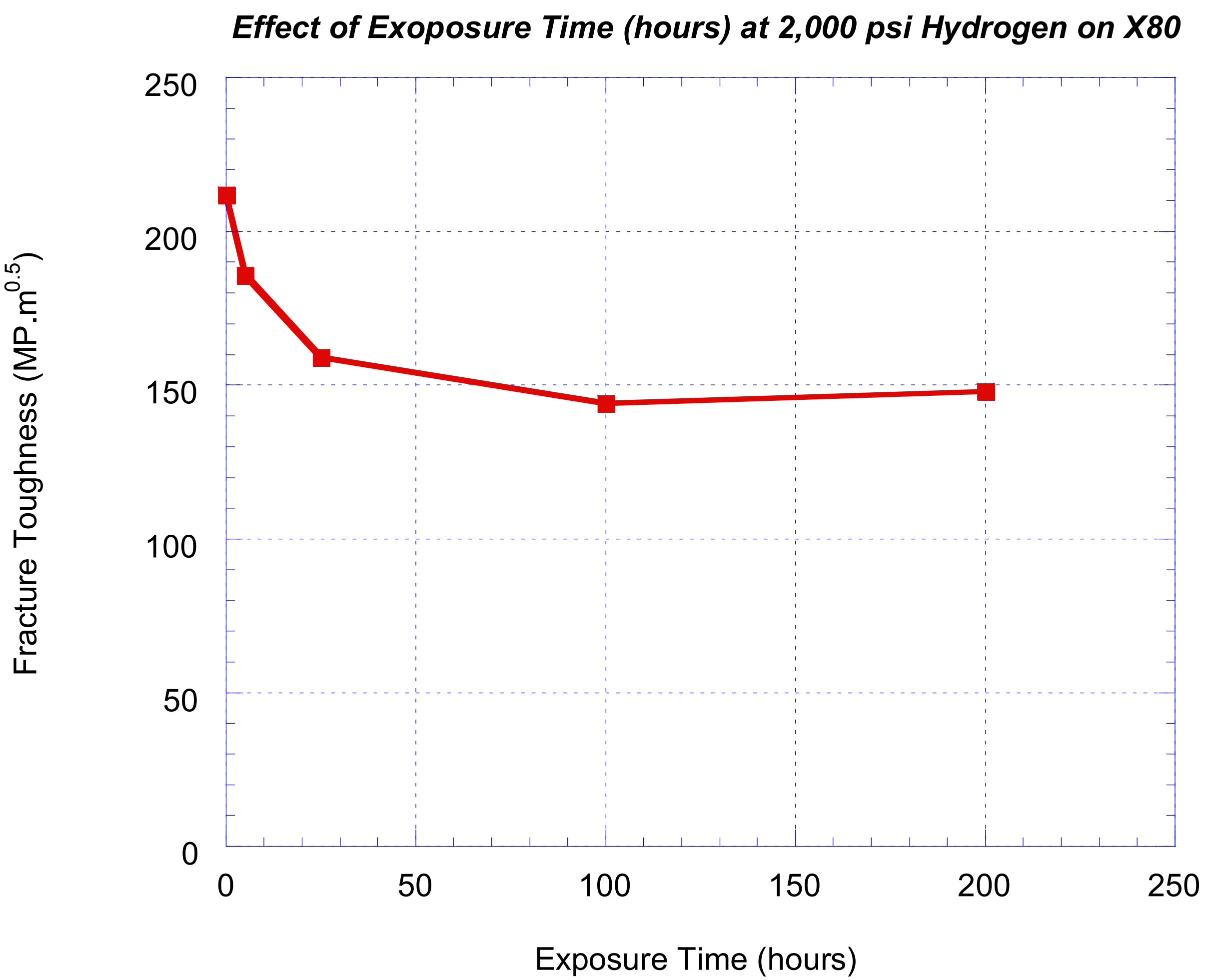








Technical Accomplishments/Progress/Results: *In-Situ* SSM Testing System



Technical Accomplishments/Progress/Results:

In-Situ SSM Testing System

- The ABI-determined fracture toughness of X80 pipeline steel decreased by 12.3%, 25%, 32%, and 30% after 2,000 psi hydrogen exposure times of 5, 25, 100, and 200 hours. It appears that the reduction in fracture toughness saturates at 100 h for the 9.5-mm (0.375-inch) thick sample.

- This compared well with the 49% reduction in fracture toughness of 0.5T CT sample tested in an autoclave by Praxair. The complete immersion in hydrogen is more severe than actual hydrogen pipeline transmission application. The ABI hydrogen chamber better simulates the real pipeline steel application. Increase in tensile properties was very small for X80 pipeline steel and no changes were measured for other grades.

- No reduction in fracture toughness was observed for ABI disc samples manufactured from Grades B, X52, and X70 exposed to hydrogen pressure with the X80 steel.

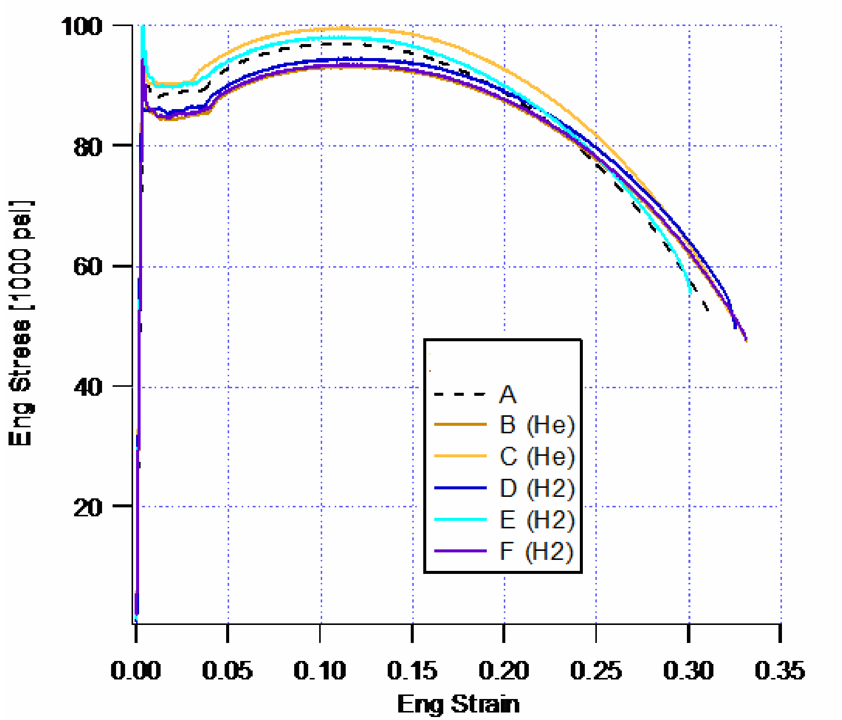
- The ABI test methods provide a nondestructive/in-situ means to monitor hydrogen effects on fracture toughness properties of in-service pipelines.

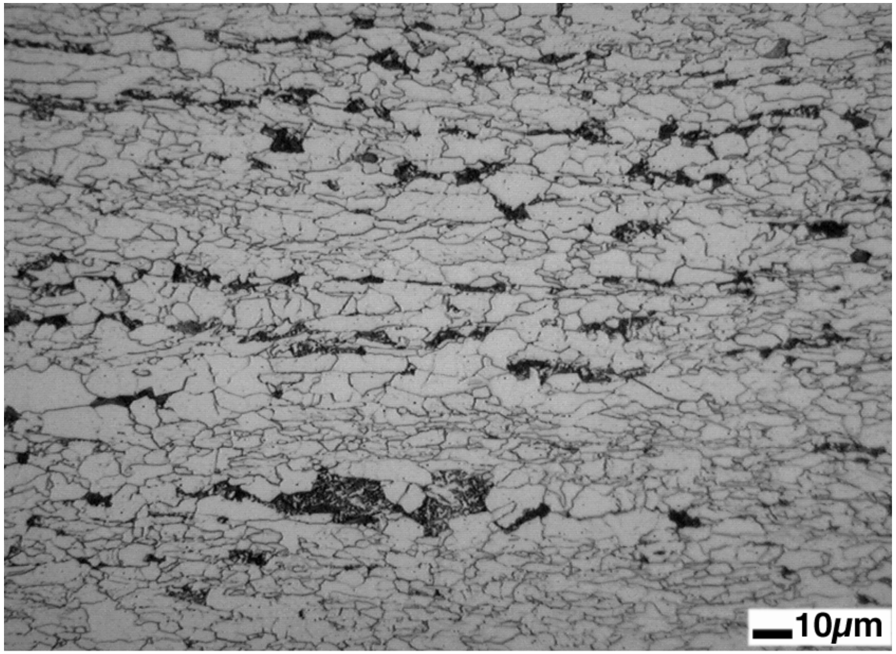
- Samples need to be evaluated for characterization of alloy and microstructural design, especially the Praxair supplied samples.

Technical Accomplishments/Progress/Results - Hydrogen Embrittlement of Steels was Evaluated using *Ex-Situ* Tensile Tests

- Samples were tested at Sandia National Laboratory, Livermore by Dr. Brian Somerday for their tendency for embrittlement using
  - *Ex-situ* high-pressure hydrogen charging, and
  - Tensile testing
- X-70 and X-80 pipeline steels were tested for hydrogen embrittlement using tensile tests after exposure to 20,000 psi hydrogen at 100^{o}C for 8 days
- To account for any temperature effects, companion set of specimens was tested after exposure to 5,000 psi helium at 100^{o}C for 8 days
- Tensile tests were conducted ex-situ in air after removing the samples from the hydrogen atmosphere
- Amount of hydrogen trapped within the sample after charging IS NOT KNOWN
  - Hydrogen out-diffusion would have occurred during cool-down and testing since no barrier coating was applied to the samples to reduce hydrogen degassing
  - Effect of oxide layers on decomposition of diatomic hydrogen and dissolution of hydrogen in steels has not been accounted for (the effect of oxide barriers is not known)

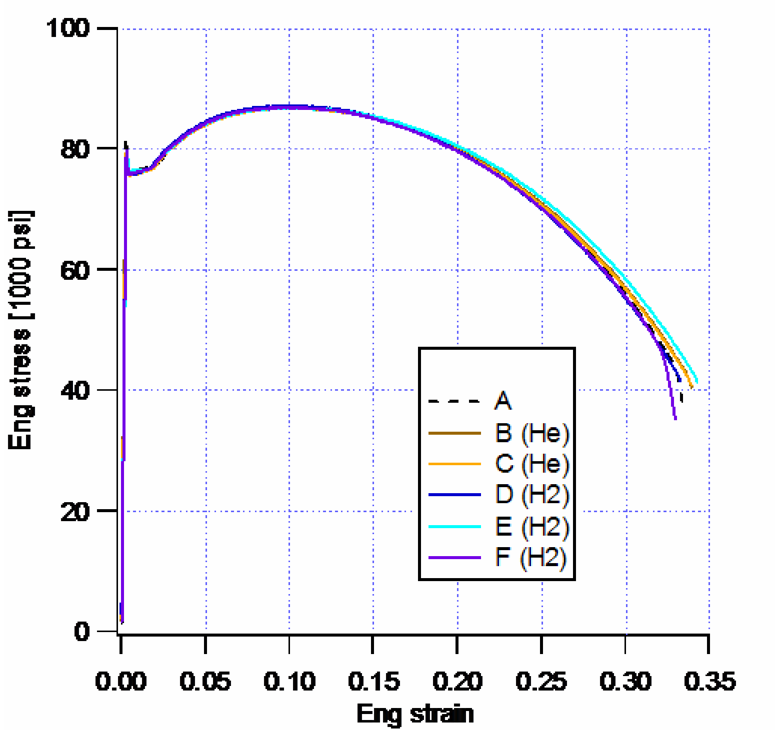
Technical Accomplishments/Progress/Results - Effect of Hydrogen on the Mechanical Properties of Steel A

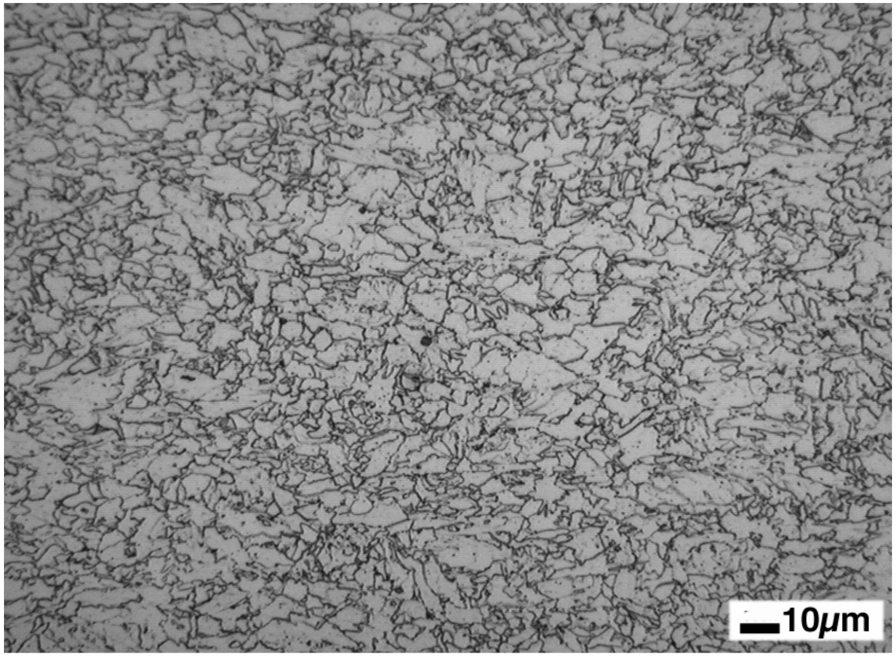




Microstructure: Ferrite + Pearlite
Yield Stress: Intermediate
Note stress- strain curves variability

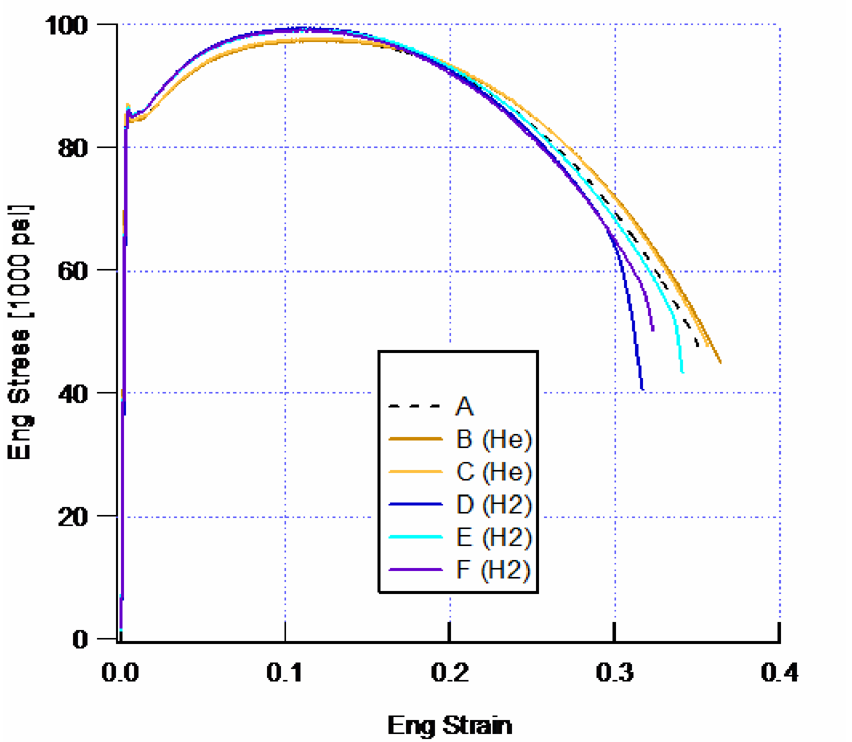
Technical Accomplishments/Progress/Results - Effect of Hydrogen on the Mechanical Properties of Steel B

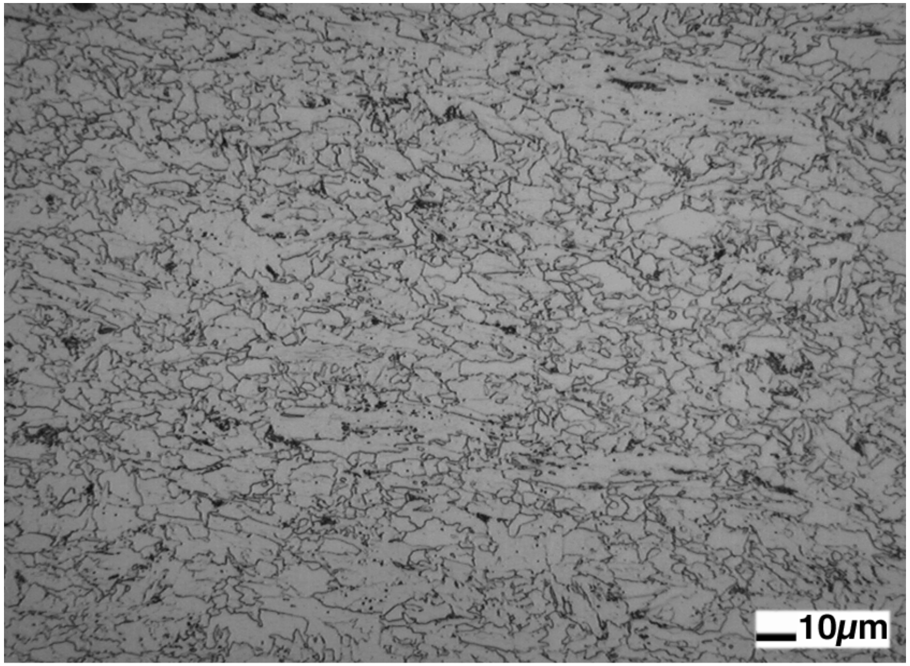




Microstructure: Ferrite + Acicular Ferrite
Yield Stress: Low
Note consistent stress-strain curves

Technical Accomplishments/Progress/Results - Effect of Hydrogen on the Mechanical Properties of Steel C





Microstructure: Ferrite/acicular ferrite + small quantity pearlite
Yield Stress: High
Note stress-strain curve with slight variability

Technical Accomplishments/Progress/Results - Observations on Hydrogen Embrittlement of Selected Steels

- Within the limited experimental results available, the following observations can be made:
  - Some trends related to yield strength can be observed but need to be more carefully studied
  - The magnitude of the observed effect is small compared to other limited data available in the literature
- The following comments can be made regarding mechanical testing to study hydrogen embrittlement
  - It would be preferable to ensure that the hydrogen is trapped in the sample using a barrier coating/plating
  - Surface condition of the sample is very important in ensuring that it is representative of real world conditions
  - Barrier layers may prevent hydrogen from entering the sample during testing giving potentially incorrect results

Technical Accomplishments/Progress/Results - Guidance For Future Hydrogen Embrittlement Testing

- Include non-microalloyed steels in the testing for comparison

- Future work will focus on ensuring that hydrogen out-diffusion is minimized and the hydrogen is trapped within the sample
  - Copper plating has been used before as an effective barrier

- Mechanical testing will be carried *in-situ* in high pressure hydrogen atmosphere
  - Particular attention will be paid to surface preparation to ensure that hydrogen will permeate the specimen

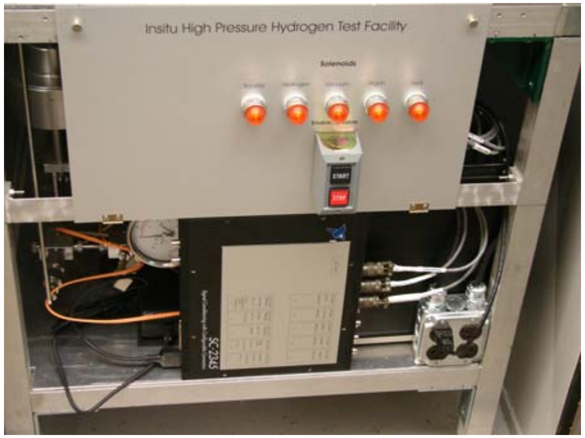
Technical Accomplishments/Progress/Results – Glassy Coating on Pipeline Steel

- After down-selection, melted 5 customized glass compositions, and prepared precursors for coating processes
- Identified and pre-evaluated low-cost approaches to coat the inside of steel tubes (paint-on-burn-in, others)
- Test-coated available, flat pipeline-steel samples to determine process parameters, and compatibility of the glass with the steel substrate

→ Thin, dense and crack/pit-free coatings obtained in a multi-step, modified enamel process

→ Coatings exhibit good adherence, but can be removed by sandblasting

Technical Accomplishments/Progress/Results – Most System Components for High Pressure Testing System are Ready at ORNL



Future Work

Remainder of FY 2007 (subject to level and availability of funding)

- **Steels**
  - Complete assembly of equipment for *in-situ* mechanical testing of materials in high hydrogen pressures along with setting up associated safety measures and controls at ORNL.
  - Begin measurement of mechanical properties and hydrogen embrittlement characteristics of down-selected steels using traditional mechanical testing.
  - Continue thermodynamic, and kinetic modeling of initial down-selected steel compositions.
  - Begin permeation testing at University of Illinois of Alloy's A, B, C, and D in un-coated and coated conditions.
  - Initiate testing and characterization of samples of commercial grade long seam pipeline welds that have been recently secured.

- **Coatings**
  - Refine glass coating process for required machined test samples.
  - Characterize glass coating properties used for testing.
  - Glass coat Alloy A, B, C, and D for high pressure hydrogen testing at ORNL and University of Illinois.

- **Financial Analysis**
  - Evaluate use and implementation of actual cost numbers as supplied by corporate partners.

Future Work

- **FY2008 (subject to level and availability of funding)**:
- **Steels**
  - Complete measurement of mechanical properties and hydrogen embrittlement characteristics of down-selected steels using traditional mechanical testing and ABI tests
  - Complete thermodynamic, and kinetic modeling of initial down-selected steel 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.
- **Coatings**
- **Financial Analysis**

Project Summary

Relevance: Steel is currently the most economical approach to energy delivery and distribution. Alloy design and subsequent microstructures are key to resistance to hydrogen embrittlement in steels.

Approach: Eight different alloy/microstructure designs representing, older pipeline steels, current commercially used microalloyed pipeline steels and alternative alloy/microstructure designed steels have been chosen and secured for testing. Glass and oxide barrier coatings will be evaluated for effectiveness in high pressure hydrogen. Financial analysis modeling will determine most cost-effective approach.

Technical Accomplishments and Progress: Characterization of mechanical properties and microstructure is near completion. Initial high pressure hydrogen tensile testing of 3 of the commercial pipeline steels representing 3 different microstructures has been completed with various degrees of variability within the stress-strain curve noted. Samples have been successfully machined for hydrogen testing and glass coating. Chemical composition of glass coatings and compatibility with steel substrate has been evaluated and processing finalized for testing. In-situ testing equipment built for high pressure hydrogen testing has been initially used on two pipeline alloy designs. NACE HIC Solution A testing has been completed on the four selected pipeline alloys. Actual pipeline construction costs have been reviewed.

Technology Transfers and Collaborations: Active project partnerships with key industry players; Oregon Steel Mils, Columbia Gas of Kentucky, Schott North America, Chemical Composite Coatings, Intl., Hatch Moss McDonald, Advanced Technology Corporation, ASME, DGS Metallurgical Solutions, Inc.

Proposed Future Research: Testing of alloy/microstructures and coatings will be done in the completed ORNL testing facility. Permeation testing at the University of Illinois of un-coated and coated alloys will be done. In addition, evaluation of alternative alloy/microstructures along with seam and circumferential welding consumables will conducted.

Contacts

Dr. Subodh K. Das
SECAT Inc.
(859) 514-4989
sdas@secat.net

Dr. G. Muralidharan
Oak Ridge National Laboratory
(865) 574-4281
muralidhargn@ornl.gov

Douglas G. Stalheim
DGS Metallurgical Solutions, Inc.
(360) 713-2407
dgstalheim@dgsmet.com