DOE Hydrogen Program

Materials Solutions for Hydrogen Delivery in Pipelines

Doug Stalheim

Presenting on Behalf of

Secat, Inc.

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Project ID: PD18

Overview

Timeline

- Project start date: 05/2005
- Project end date: 09/2009
- Percent complete: 25%

Budget

- Total project funding
  - $1650K (DOE share)
  - $1110K (contractor share)
- Funding for FY 07: $200K
- Funding for FY 08: $350K

Barriers and Targets

Barriers addressed

High capital cost and Hydrogen Embrittlement of Pipelines

Technical Targets (2017):

– Capital cost ($490K/Mile Transmission)

– 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**
- **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**

Objective and Deliverables

Objective:

- Develop materials technologies to minimize embrittlement of steels used for high-pressure transport of hydrogen

Deliverables:

- Identify steel compositions/microstructures suitable for construction of new pipeline infrastructure
- Develop barrier coatings for minimizing hydrogen permeation in pipelines and associated processes – **ON HOLD per DOE**
- Understand the economics of implementing new technologies

Known/Unknown

- **Known**
  - Variability of microstructure within a grade i.e. not all X52, X70, etc. is created equal
  - Disassociation of H_2 to H required
  - Disassociation causes – Corrosion, Partial Pressures
  - Surface oxide layers can inhibit diffusion of hydrogen into the steel
  - H migrates/collects in area of high residual stress (50% of residual stress due to microstructure mismatch, inclusions, thermal, mechanical)
- **Unknown**
  - H_2 embrittlement of steels/welds in high pressure dry gaseous H_2
  - Effect on steel metallurgical microstructures in high pressure dry gaseous H_2
  - Effectiveness of non-metallic coatings in minimizing H_2 issues
  - Economics of technical solutions not qualified
  - Is common X70 microstructure suitable in high pressure dry gaseous H_2 (Volume fraction? Banding? Moisture/corrosion?)
  - Suitability of alternative microstructures in high pressure dry gaseous H_2 (Volume fraction? Banding? Moisture/corrosion?)

Major Tasks

Task 1: Evaluate hydrogen embrittlement characteristics of existing commercial pipeline base steels/microstructures and welds under high-pressure hydrogen gas

Task 2: Evaluate hydrogen embrittlement characteristics of existing commercial alternative alloy/microstructure steels under high-pressure hydrogen gas

Task 3: Develop Alternate Alloys/microstructure and welding consumables and Evaluate Hydrogen Embrittlement

Task 4: Financial Analysis and Incorporation into Codes and Standards

Note – Tasks related to coatings have been placed on hold and are not represented here.

Progress To Date

a) Four (4) commercial pipeline steels have been down-selected – Task 1

- Majority of the baseline pipeline steel microstructure and mechanical property data have been characterized
- Commercial X70 pipeline welds have been secured for future work
- Two (2) traditional screening tests have been explored
- *In-situ* ABI test has been developed
- Processing techniques developed for glassy coatings
- Down-selected steel composition has been coated
  - For evaluation in high pressure hydrogen gas
  - Evaluation of coating technique effect on steel microstructure.

b) Two (2) commercial abrasion resistant/structural steels have been down-selected – Task 2

- Low carbon-high alloy capable of producing 100% bainite or 100% martensite microstructures (dependant on processing) with good toughness
- Medium carbon-high alloy capable of producing 100% bainite or 100% martensite microstructures (dependant on processing) with good toughness

Down-selected Commercial Pipeline Steel Compositions – Task 1

Grade*	Code	Carbon	Microstructure	Comment
X70 Std	A	0.08	Ferrite/Pearlite	Baseline
X70/X80	B	0.05	Ferrite/Acicular Ferrite	Potentially Good
X70/X80	C	0.04	Ferrite/Acicular Ferrite/Sm Pearlite	Potentially Good
X52/X60 HIC	D	0.03	Ferrite/Acicular Ferrite	Potentially Best

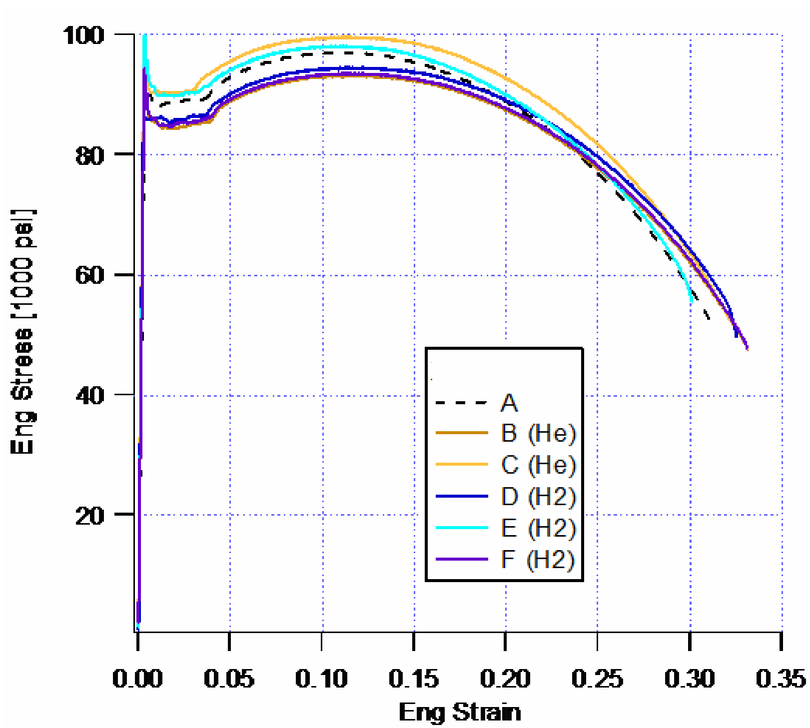
*Note that all are commercially available pipeline base steels utilizing microalloying technology.

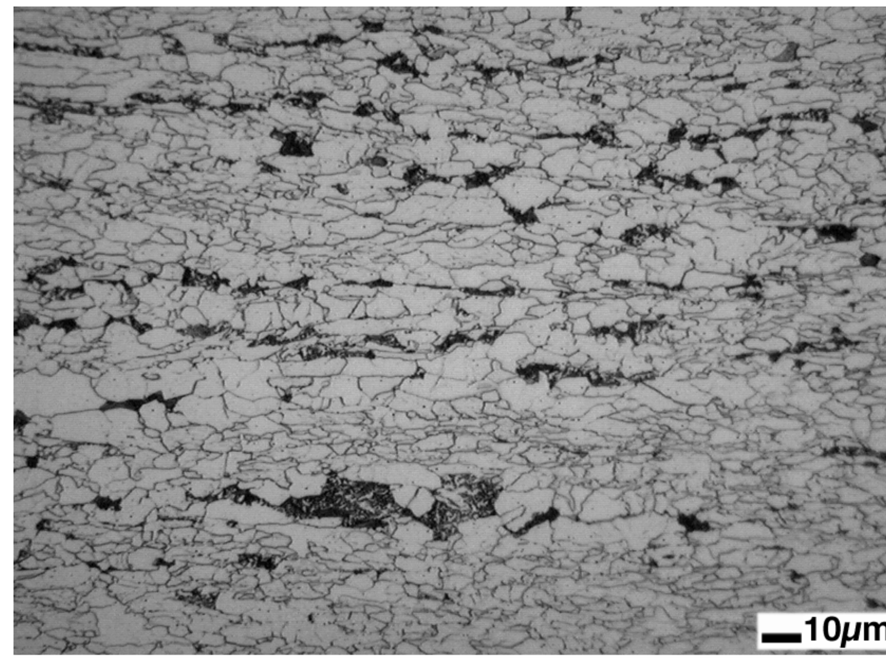
Down-selected Commercial Abrasion Resistant/Structural Alternative Steel Compositions/Microstructures – Task 2

Grade*	Code	Carbon	Alloy	Microstructure	Comment
100 KSI Yield Strength	E	0.08	Mn, Ni, Nb, B, Ti	100% Bainite or Martensite dependent on processing	Potentially Good
Abrasion Resistant 400 BHN	F	0.15	Mn, Si, Cr, Mo, Nb, B, Ti	100% Bainite or Martensite dependent on processing	Potentially Good

*Note that all are commercially available structural/abrasion resistant base steels utilizing solute solution strengthening and boron/microalloying technology

Effect of Hydrogen on the Mechanical Properties of Steel A – Ex-situ Testing





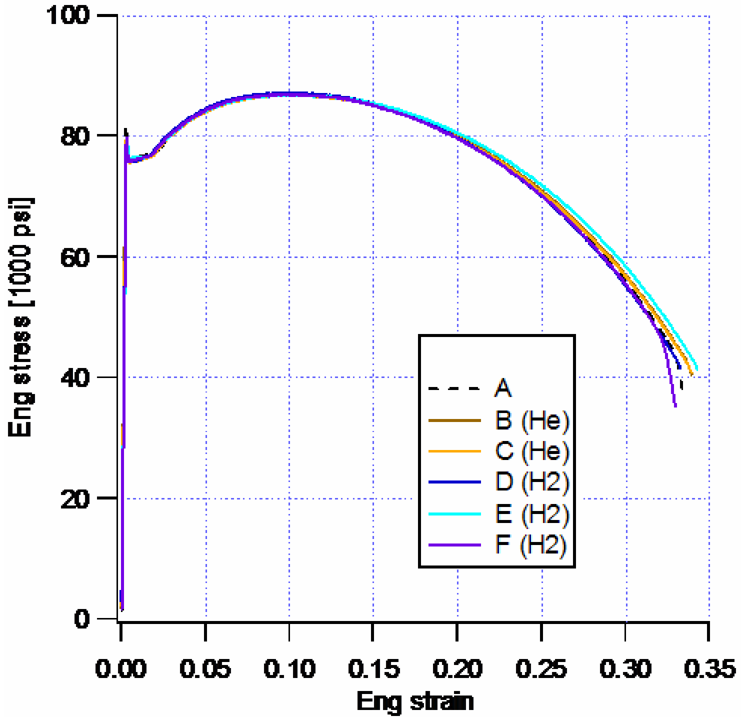
20 KSI H2 @ 100 °C for 8 days
5 KSI He @ 100 °C for 8 days
Strain rate 10^{-4} in/in/sec

Ferrite + Pearlite

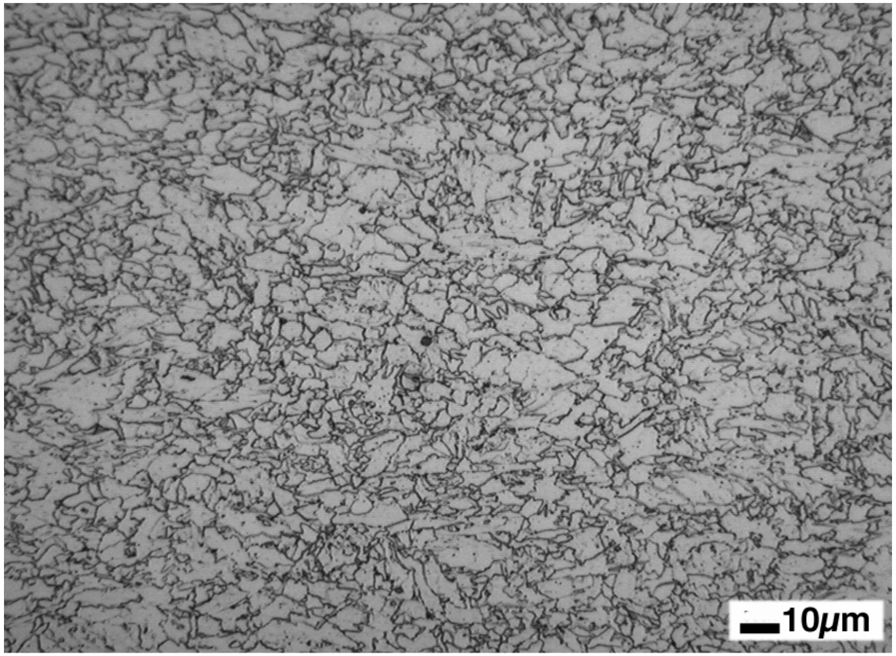
Surface to ¼ thick – 4.13% volume fraction pearlite
¼ thick to centerline – 8.40% volume fraction pearlite
Centerline – 6.90% volume fraction pearlite

Note the relatively large variability of stress-strain curves

Effect of Hydrogen on the Mechanical Properties of Steel B – Ex-situ Testing



20 KSI H2 @ 100 °C for 8 days
5 KSI He @ 100 °C for 8 days
Strain rate 10^{-4} in/in/sec

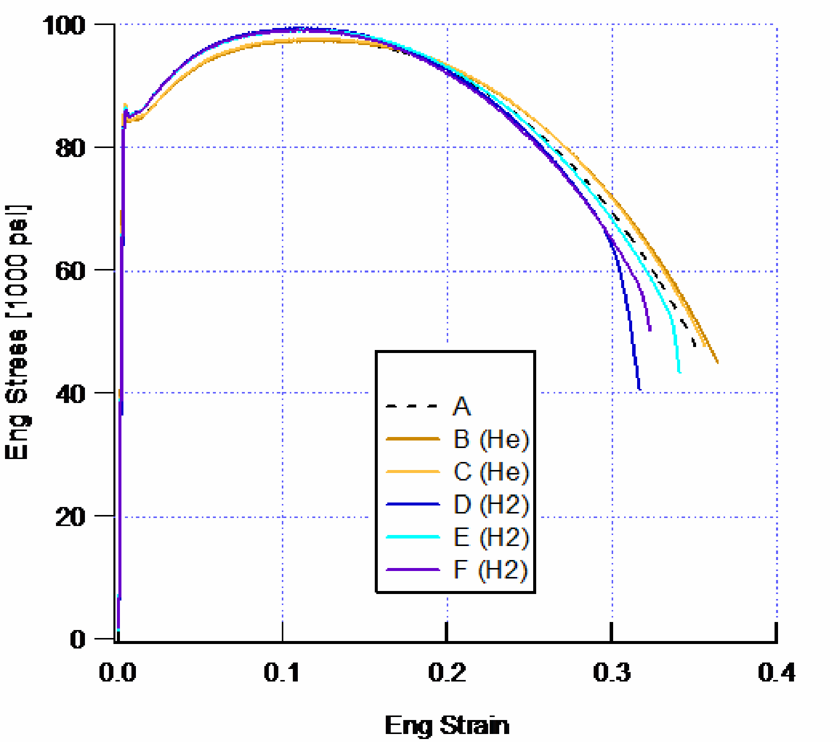


Ferrite + Acicular Ferrite

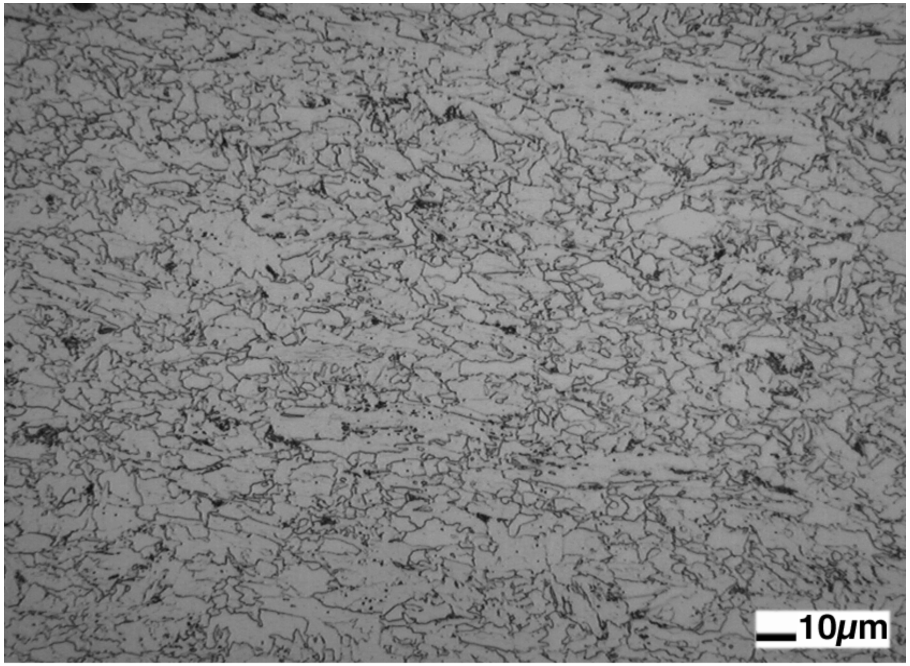
Surface to ¼ thick – Acicular ferrite TBD by TEM
¼ thick to centerline – Acicular ferrite TBD by TEM
Centerline – Acicular ferrite TBD by TEM

Note the relatively small variation in the stress-strain curves

Effect of Hydrogen on the Mechanical Properties of Steel C – Ex-situ Testing



20 KSI H2 @ 100 °C for 8 days
5 KSI He @ 100 °C for 8 days
Strain rate 10^{-4} in/in/sec



Ferrite/acicular ferrite + sm pearlite

Surface to ¼ thick – AF TBD by TEM, pearlite TBD
¼ thick to centerline – AF TBD by TEM, pearlite TBD
Centerline – AF TBD by TEM, pearlite ≈ 3%

Note intermediate variability in the stress-strain curves

NACE Hydrogen Induced Cracking (HIC) Test

- Evaluates resistance of pipeline and pressure vessel plate steels to Hydrogen Induced Cracking (HIC) caused by hydrogen adsorption through a corrosive mechanism

- Cracks that develop in the microstructure are evaluated transverse to the rolling direction

- UNSTRESSED test specimens are immersed in one of two H_2S containing solutions for 96 hours – Solution A (Low pH – more severe), Solution B (High pH – less severe)

- Test provides reproducible environments for distinguishing RELATIVE susceptibility to HIC in a relatively SHORT TIME

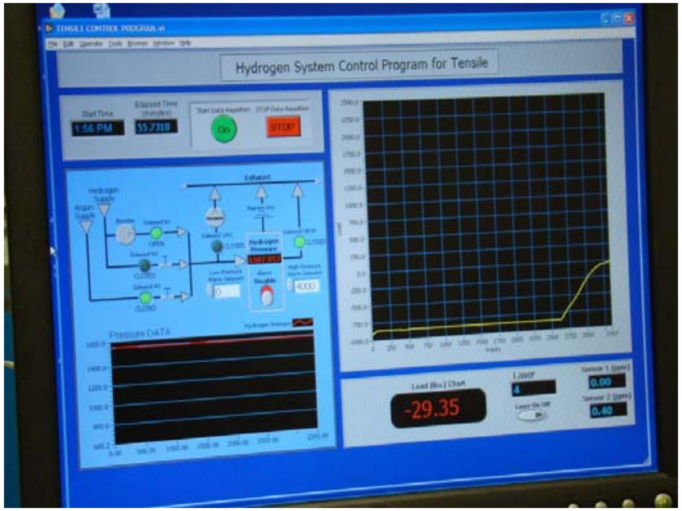
NACE HIC Testing of Selected Pipeline Steels

Alloy	Crack Length Ratio (%)	Crack Sensitivity Ratio (%)	Crack Thickness Ratio (%)
A	11.8[a]	0	0.1
B	0.4[b]	0	0
C	0	0	0
D	0	0	0

a) Cracks located at the ferrite/pearlite interface
b) Cracks located between surface and ¼ thickness and associated with cluster of non-metallic inclusions (related to ¼ thickness casting inclusion issue)

Lower numbers are desirable

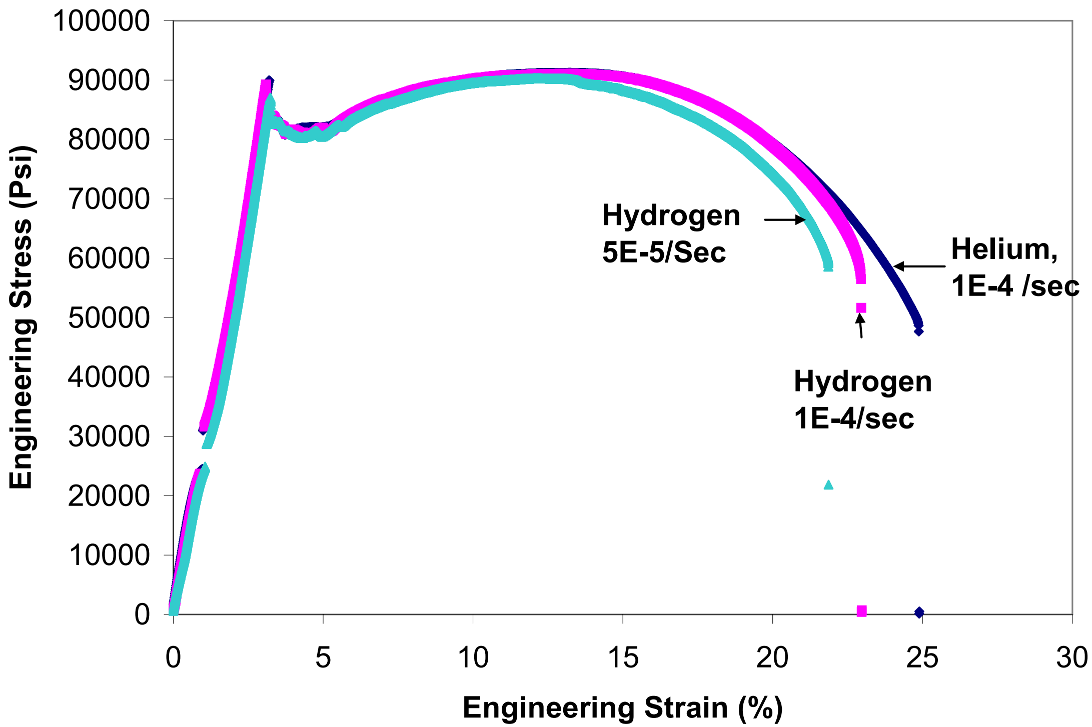
System for *in-situ* Testing in High Pressure Hydrogen is Now Fully Functional at ORNL



Key features

- Room temperature gas pressures up to 4800 psi
- Strain rates down to 1E-6/sec
- Test loads up to 4000 lbs
- Flexible specimen geometry
- Computer-controlled valves and data acquisition

Effect of Strain Rates on Stress-Strain Curves in Hydrogen Atmosphere for Alloy A



Note: Friction correction has NOT been applied

- Gas compositions used: UHP hydrogen (99.9999%), UHP Helium (99.9999%)
- Gas pressure: 1580 psi
- Presence of hydrogen decreases total strain to failure
- The decrease in total strain is a function of the strain rate used for testing

Fracture Mode of Steel A Changes in the Presence of Hydrogen

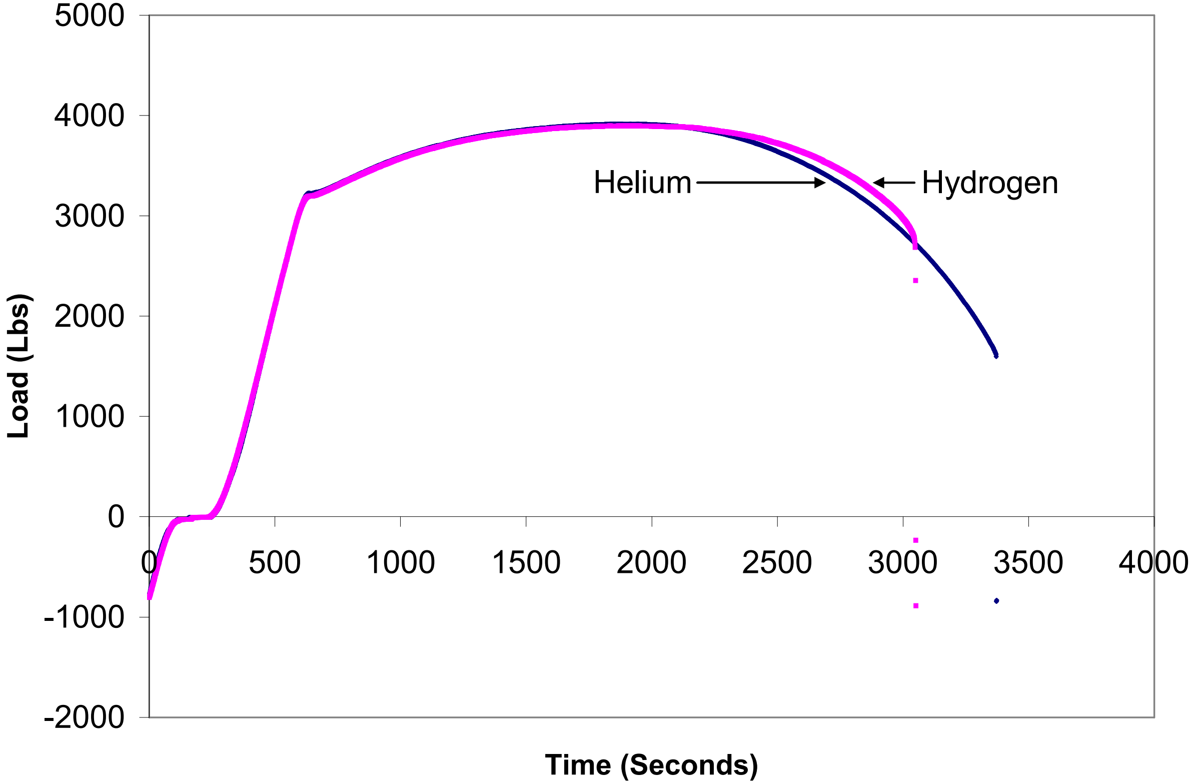
Helium

Ductile cup and cone fracture

Hydrogen

Faceted fracture surface with evidence for multiple secondary cracking

Effect of Hydrogen on Deformation Characteristics of Alloy C



- Pressure: 1580 psi, Strain rate: 1E-4 /sec
- Total elongation decreases in a hydrogen atmosphere

Fracture Mode of Steel C Also Changes in the Presence of Hydrogen

Helium

Ductile cup and cone fracture

Hydrogen

Faceted fracture surface with visible secondary cracking

Future Work

- **Steels**
  - Complete measurement of mechanical properties *in-situ* high pressure hydrogen testing of commercial pipeline steels and commercial alternative microstructures
  - Evaluate effect of different strain rates for *in-situ* testing
  - 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

- **Economic Analysis**
  - Recommend steel and coating systems for implementation
  - Evaluate economic impact of suggested materials systems

Contacts

Dr. Subodh K. Das
Secat, Inc.
(859) 514-4989
skdas@secat.net