Materials Solutions for Hydrogen Delivery in Pipelines

Secat, Inc.

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Arlington, VA

Project ID – PD047

Overview

Timeline

- Project start date: 05/2005
- Project end date: 09/2011
- Percent complete: 80%

Budget

- Total project funding
  - $1650K (DOE share)
  - $707K (contractor share)
- Funding for FY 08: $113 K
- Funding for FY 09: $281 K

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

- **ASME Standards and Technologies**
- **Chemical Composite Coatings Intl**
- **Columbia Gas of Kentucky**
- **EVRAZ - Oregon Steel Mills**
- **Schott North America**
- **DGS Metallurgical Solutions, Inc.**
- **Hatch Moss MacDonald**
- **Oak Ridge National Laboratory**
- **University of Illinois**
- **Reference Metals Company**

Objective and Deliverables

Objective:

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

Deliverables:

- **Most Important** - 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 – **ON HOLD per DOE**
- Understand the economics of implementing new technologies

Objective Relevance

- **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 no-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?)

Relevant Key Technical Barriers

- Hydrogen embrittlement of steels and welds exposed to high pressure dry gaseous H_2 is **not well understood**
- Effect of steel metallurgical microstructures on hydrogen embrittlement in a high pressure dry gaseous H_2 environment are **not known**
- Effectiveness of metallic and non-metallic coatings on minimizing H_2 embrittlement at high pressures has **not been studied**
- Economics of technological solutions to remediate the effect of hydrogen embrittlement has **not been quantified**

Milestones or Go/No-Go Decisions

Month/Year	Milestones or Go/No-Go Decisions
August 08	**Milestone:** Completed initial round of tensile testing in high pressure (800, 1600, 3000 psi) gaseous hydrogen of 4 down selected commercially available transmission pipeline steels.
September 08	**Go/No-Go Decision:** Using the scientific community recognized method for evaluation of hydrogen effect on tensile testing of reduction in area along with previous NACE testing for hydrogen cracking resistance and microstructural analysis, two of the best performing of the four down selected pipeline steels will be further evaluated with fracture toughness and fatigue testing in high pressure gaseous hydrogen. The other two alloys may be evaluated at a later date.
May 09	**Milestone:** Complete final smaller validation round of tensile testing in high pressure gaseous hydrogen of four down selected commercially available transmission pipeline steels.
December 09	**Milestone:** Completed fracture toughness and fatigue testing in high pressure gaseous hydrogen of two selected commercially available pipeline steels based on Sept. 08 Go/No-Go Decision.
December 10	**Milestone:** Finish fracture and fatigue testing of alternative commercially available steels/microstructures.

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. Focus of the project has shifted predominately to Tasks 1 and 2 and Task 4 incorporation of relevant information into Codes and Standards.

Progress To Date

a) Four (4) commercial pipeline steels have been down-selected, X70, X70/X80, X70/X80, X52/X60 HIC

- Majority of the baseline pipeline steel microstructure and mechanical property data have been characterized
- Commercial X70 pipeline welds available
- Two (2) traditional screening tests have been explored
- *In-situ* ABI 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 of all 4 alloys at ORNL complete
  - Two strain rates - $1x10^{-4}$, $1X10^{-5}$
  - Hydrogen vs. helium
  - 3 pressures – 800 psi, 1600 psi, 3000 psi
  - Total initial tests = 48, additional validation testing = 10, additional statistical testing of alloy A and B

Progress To Date

a) **Continued**

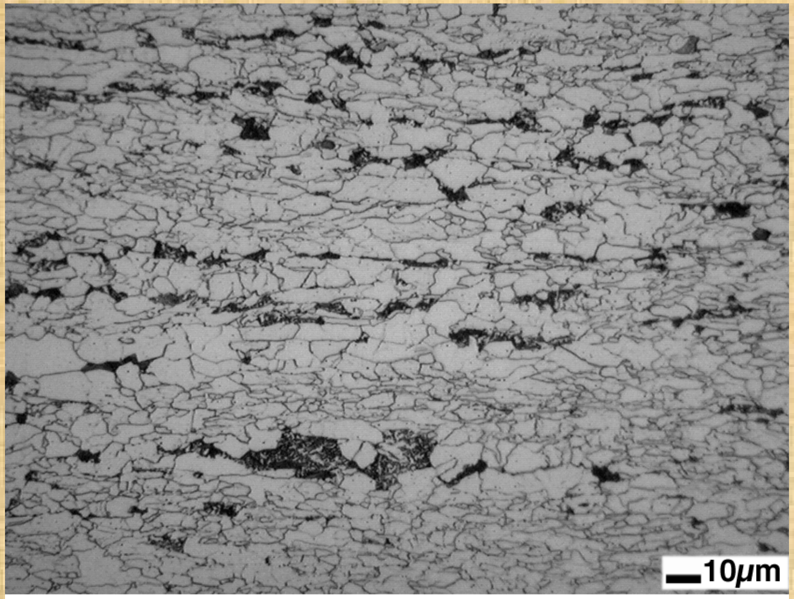
- Completed detailed microstructural characterization for the 4 selected pipeline steels.
- Completed fracture and fatigue testing completed of 2 selected pipeline steels at 800 and 3000 psi H_2 pressure at Sandia National Laboratory.

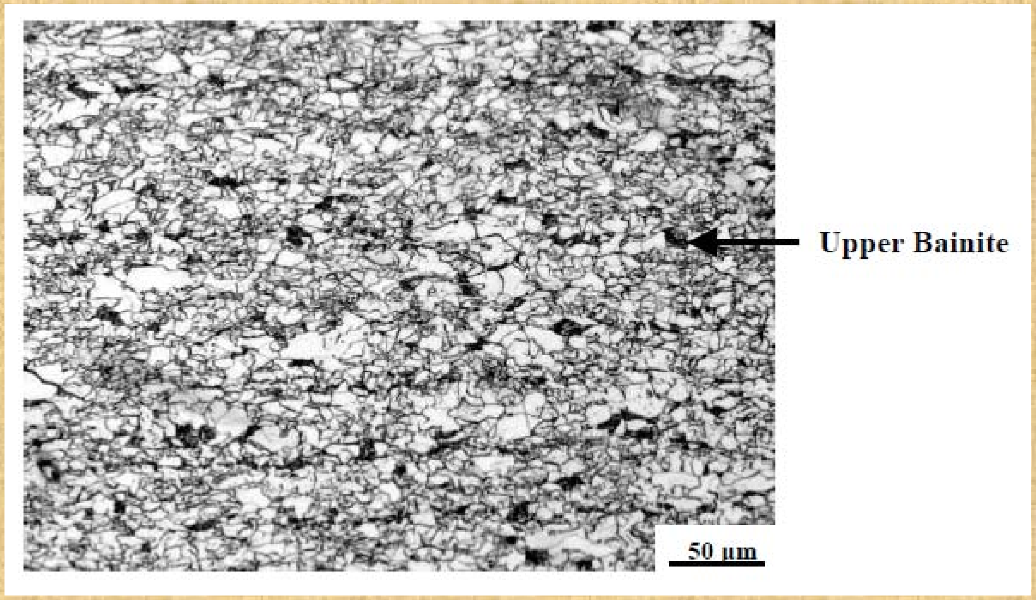
b) **Two (2) commercial abrasion resistant/structural steels have been down-selected**

- One is low carbon-high alloy capable of producing 100% bainite or 100% martensite microstructures (dependant on processing) with good toughness
- Second is medium carbon-high alloy capable of producing 100% bainite or 100% martensite microstructures (dependant on processing) with good toughness

Approach – Details of Microstructural Characterization of Steels Tested

Alloy A (X70) – Polygonal Ferrite/Upper Bainite (Upper Bainite ~ 8%)

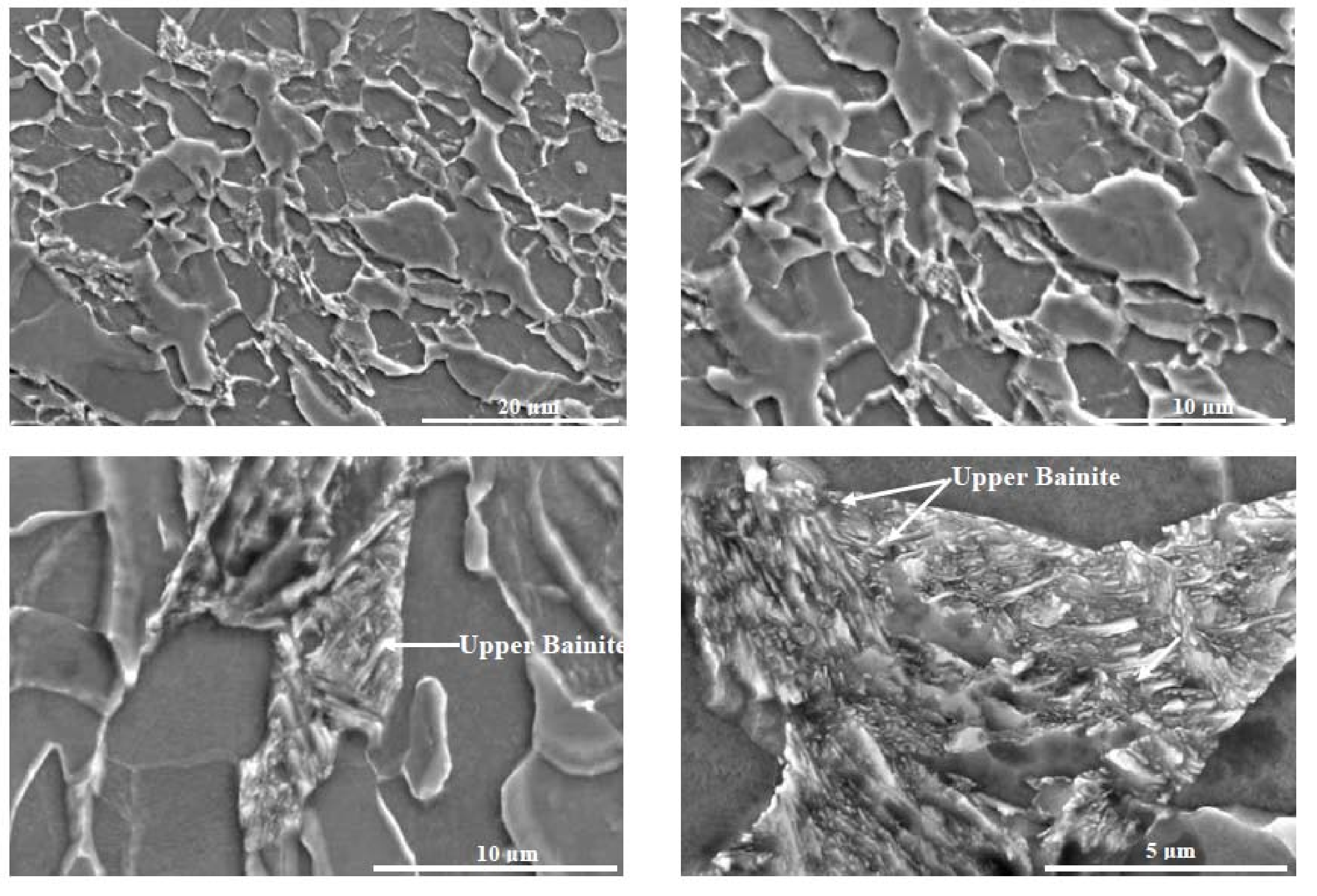




Approach – Details of Microstructural Characterization of Steels Tested

Alloy A (X70) – Polygonal Ferrite/Upper Bainite (Upper Bainite ~ 8%)

SEM Analysis



Approach – Details of Microstructural Characterization of Steels Tested

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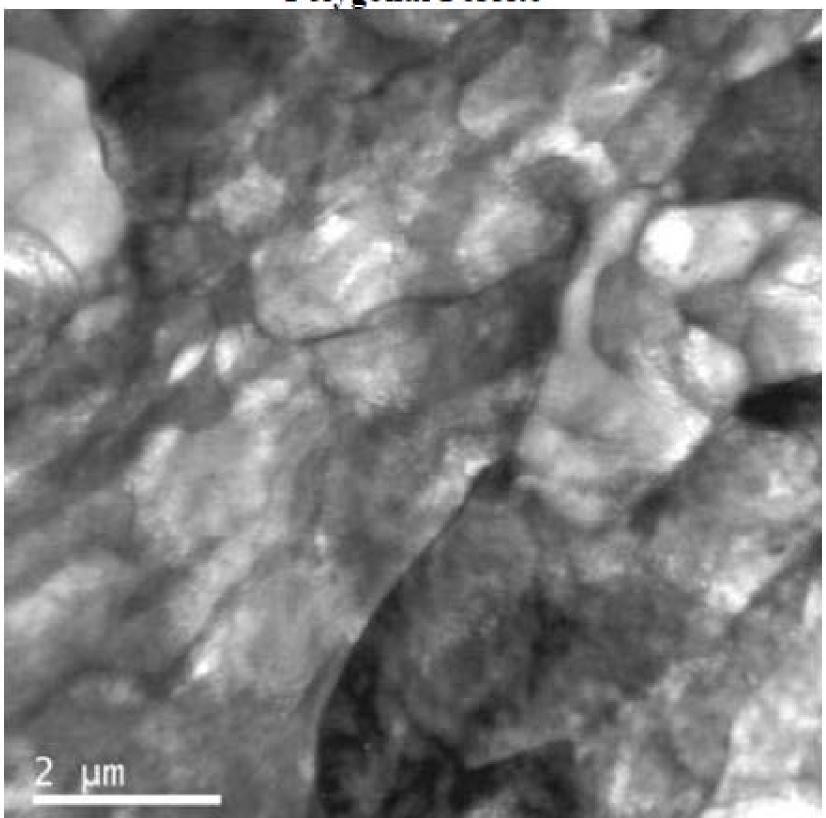
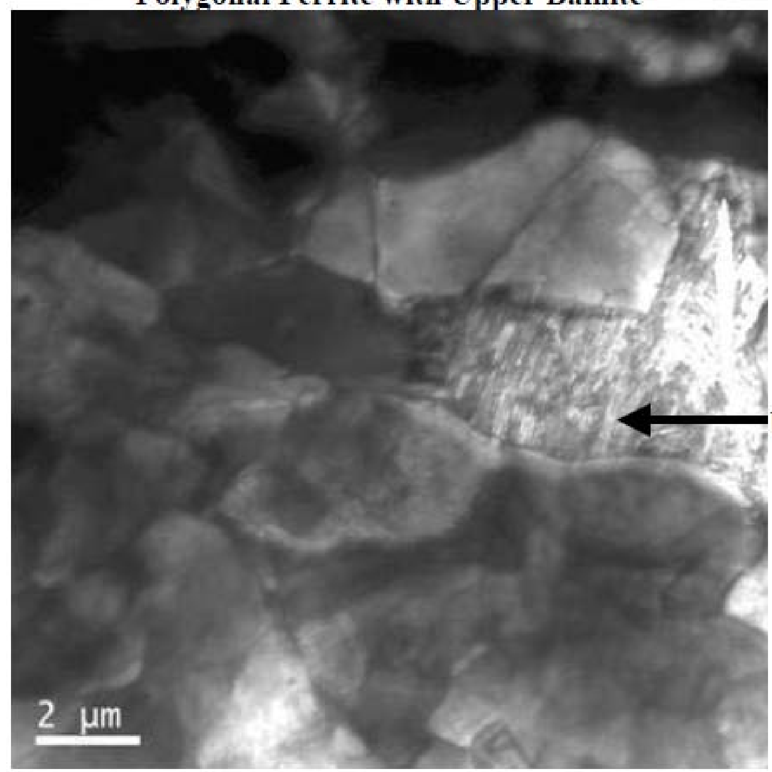
TEM Analysis

Polygonal Ferrite



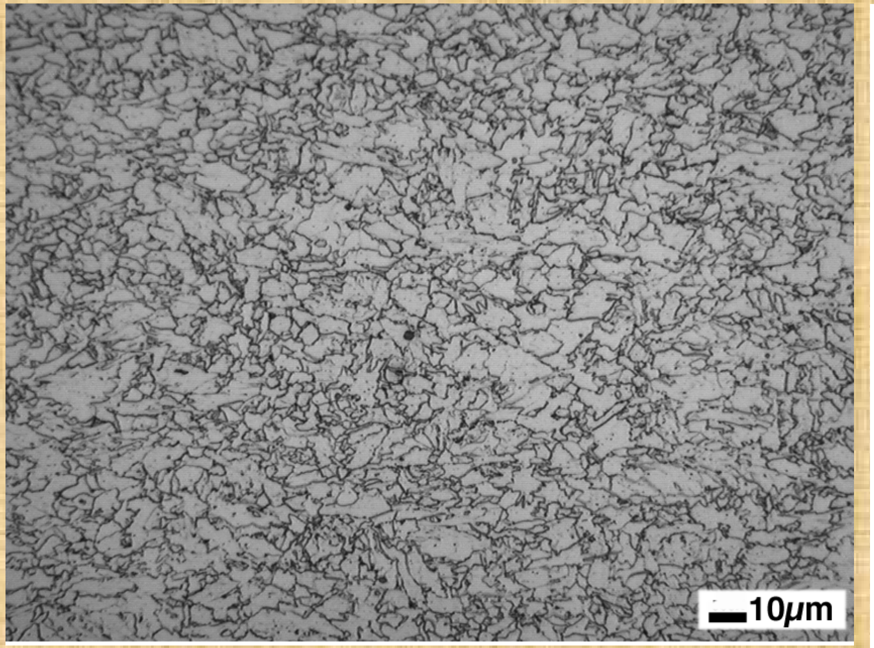
Polygonal Ferrite with Upper Bainite

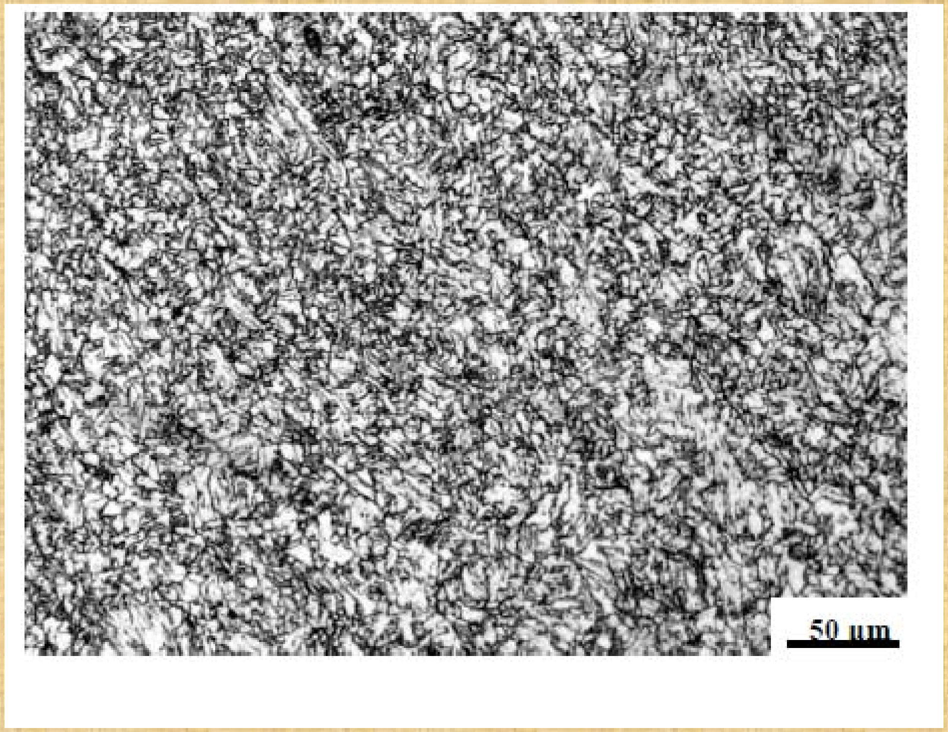


Upper Bainite

Approach – Details of Microstructural Characterization of Steels Tested

Alloy B (X70/X80) – Polygonal Ferrite/Coarse Acicular Ferrite (type of Bainite) ~ 10%, Optical Light Microscopy





Approach – Details of Microstructural Characterization of Steels Tested

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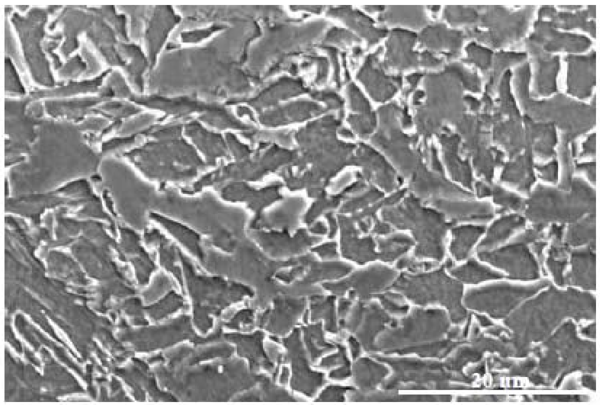
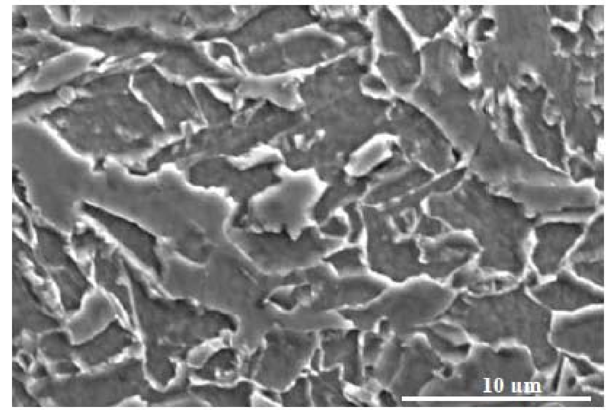
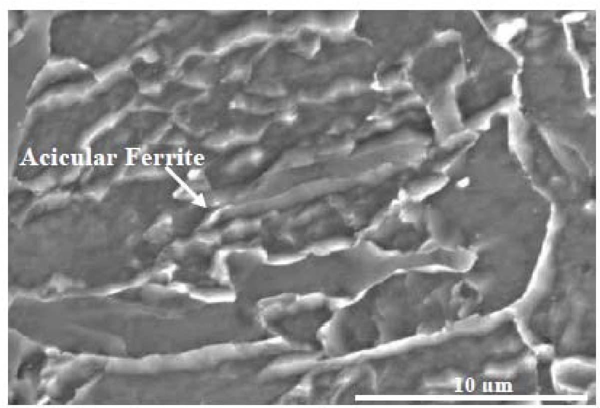


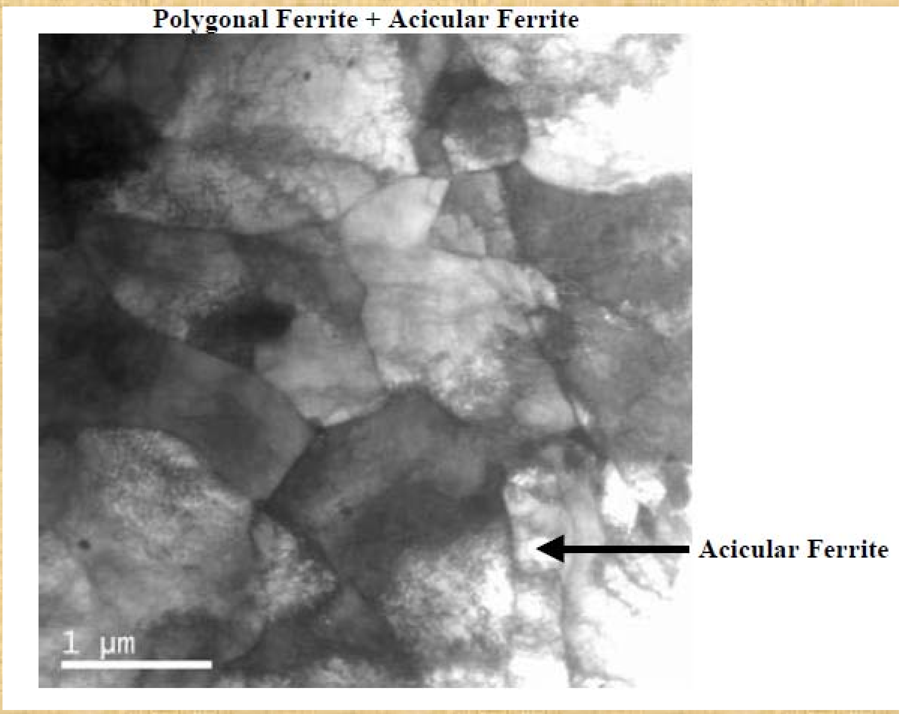


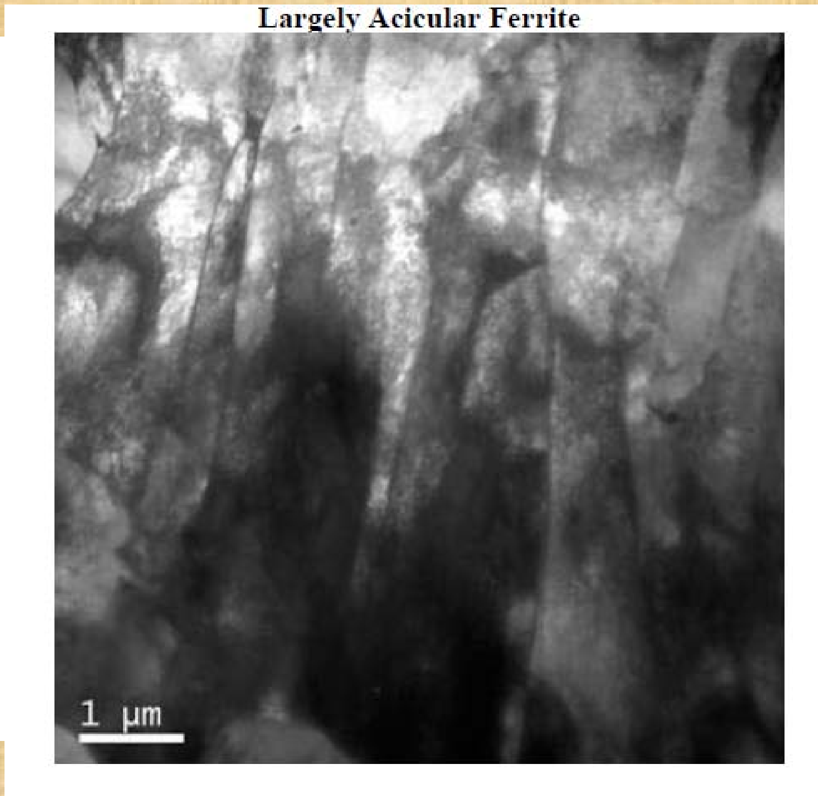


Coarse Acicular Ferrite is more apparent in TEM micrographs

Approach – Details of Microstructural Characterization of Steels Tested

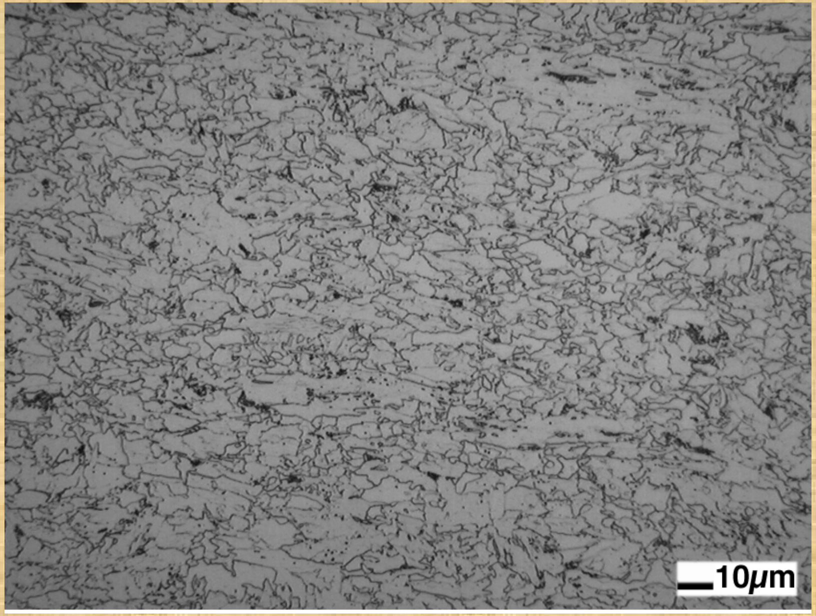
Alloy B (X70/X80) – Polygonal Ferrite/Coarse Acicular Ferrite (type of Bainite) ~ 10%, TEM Analysis

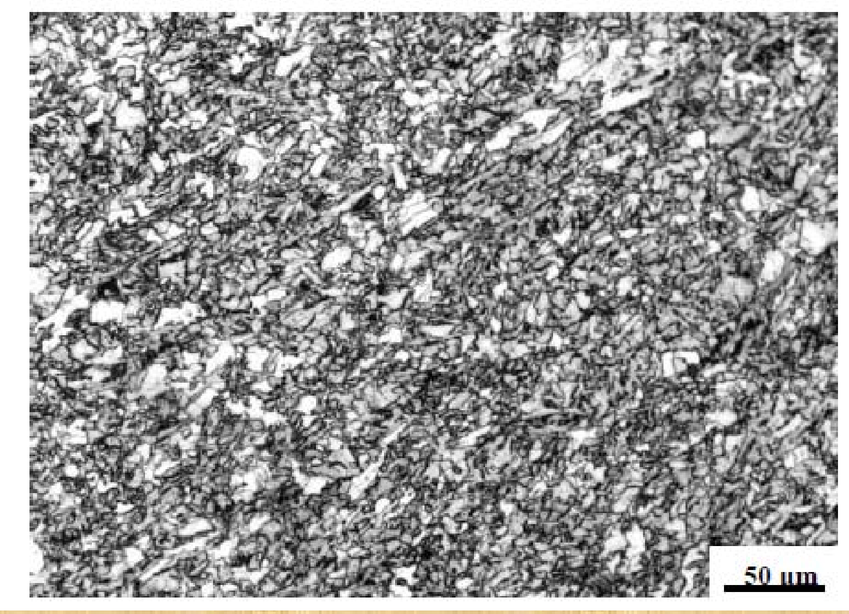




Approach – Details of Microstructural Characterization of Steels Tested

Alloy C (X70/X80) – Polygonal Ferrite/Coarse Acicular Ferrite (type of Bainite), plus Upper Bainite ~ 10%, Optical Light Microscopy





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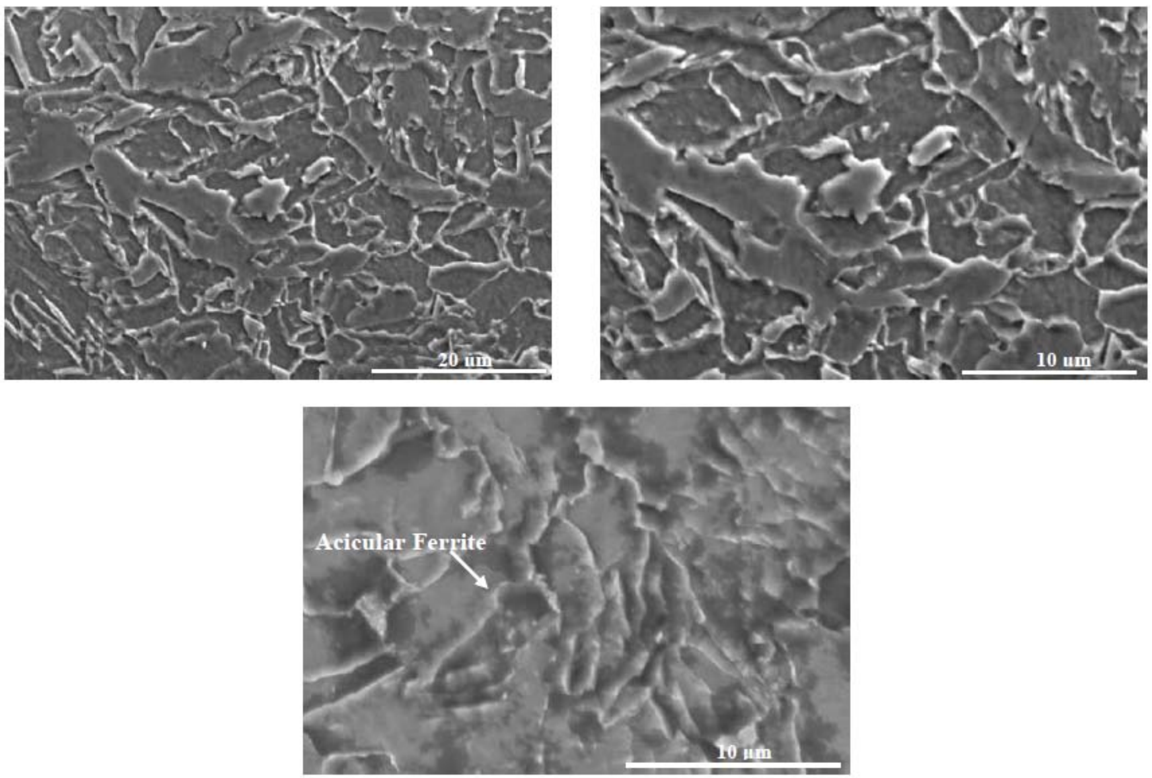

Coarse Acicular Ferrite is more apparent in TEM micrographs

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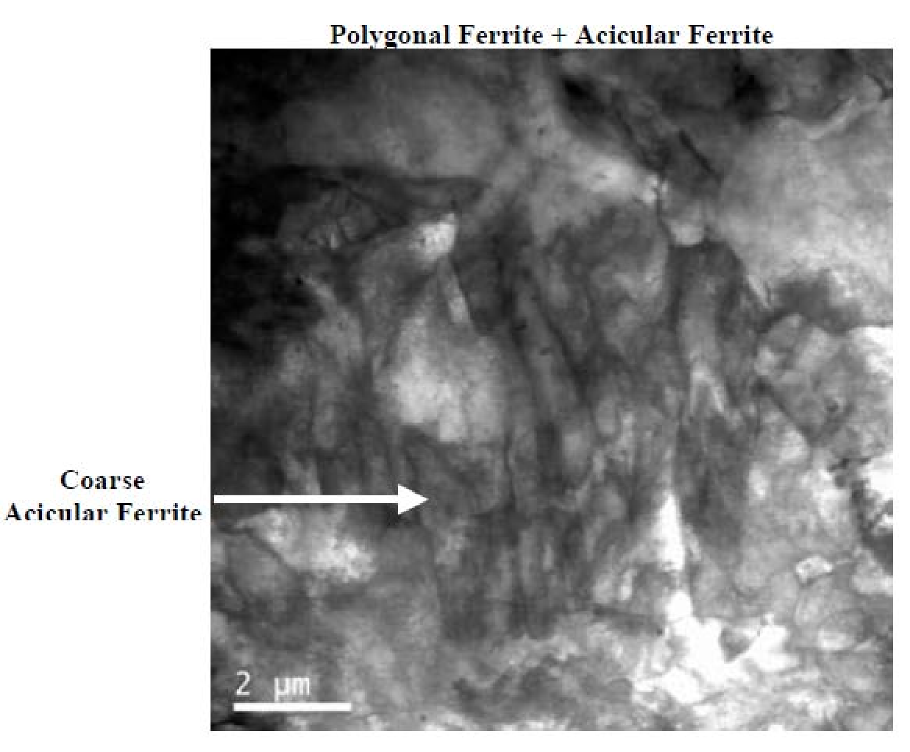
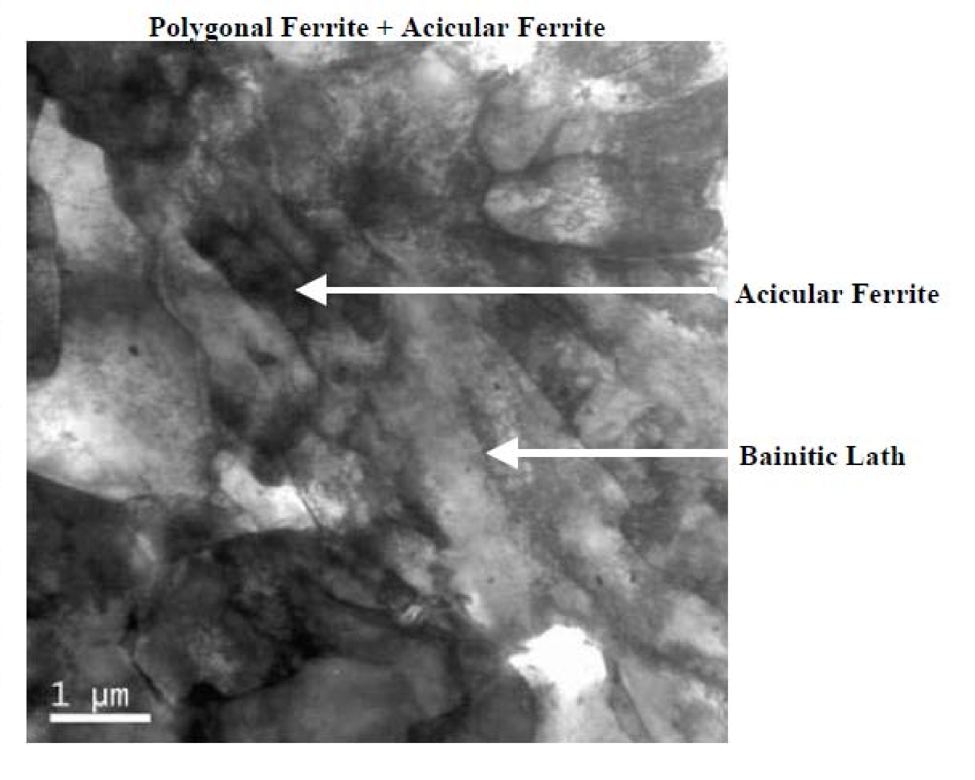
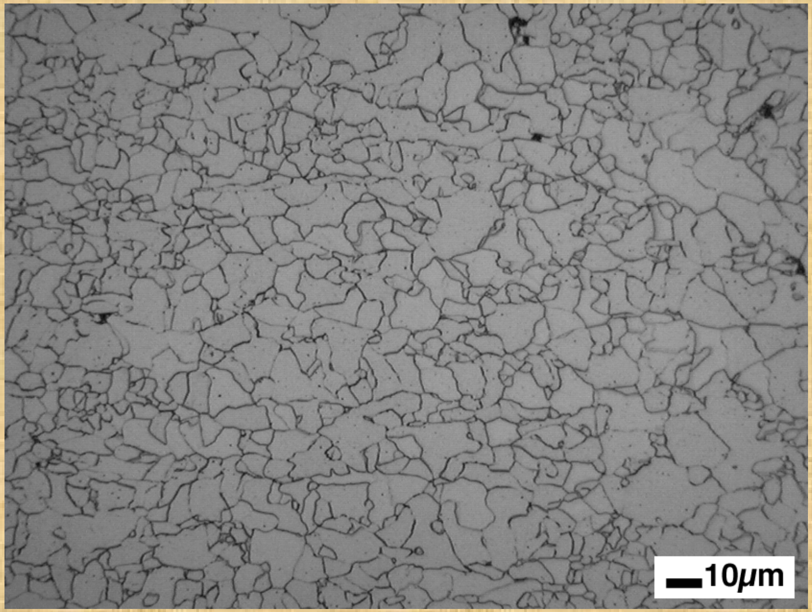


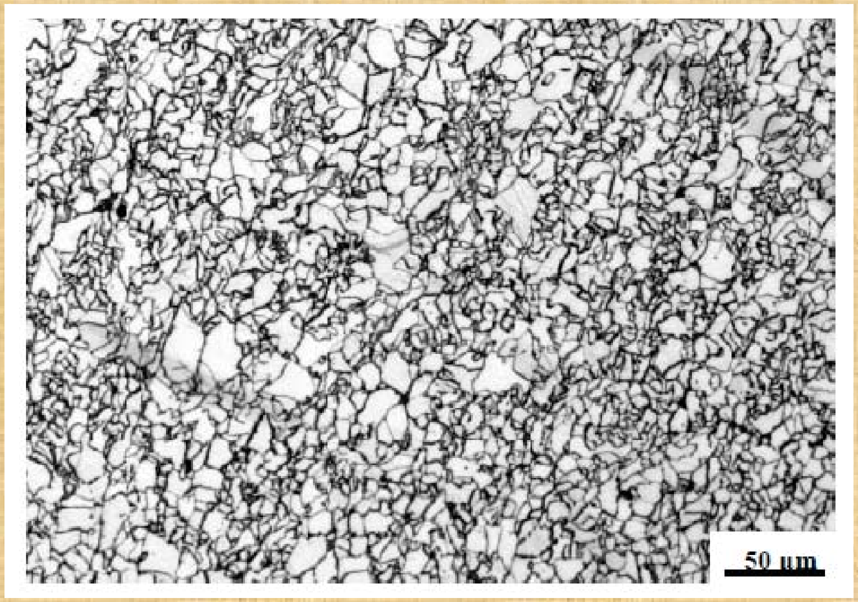


Approach – Details of Microstructural Characterization of Steels Tested

Alloy D (X52/X60 HIC) – Polygonal Ferrite – 100%

Optical Light Microscopy

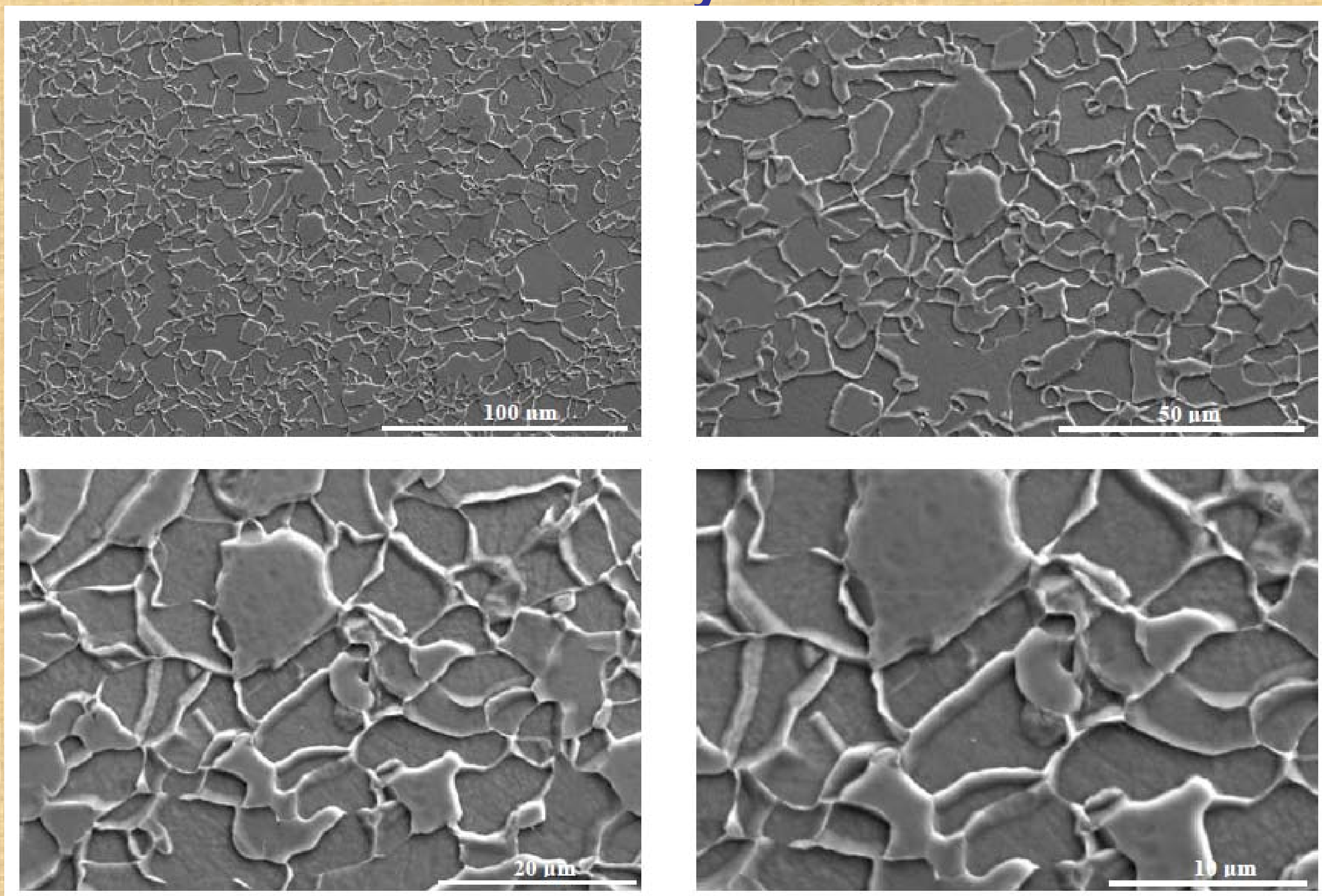




Approach – Details of Microstructural Characterization of Steels Tested

Alloy D (X52/X60 HIC) – Polygonal Ferrite – 100%

SEM Analysis



Approach – Details of Microstructural Characterization of Steels Tested

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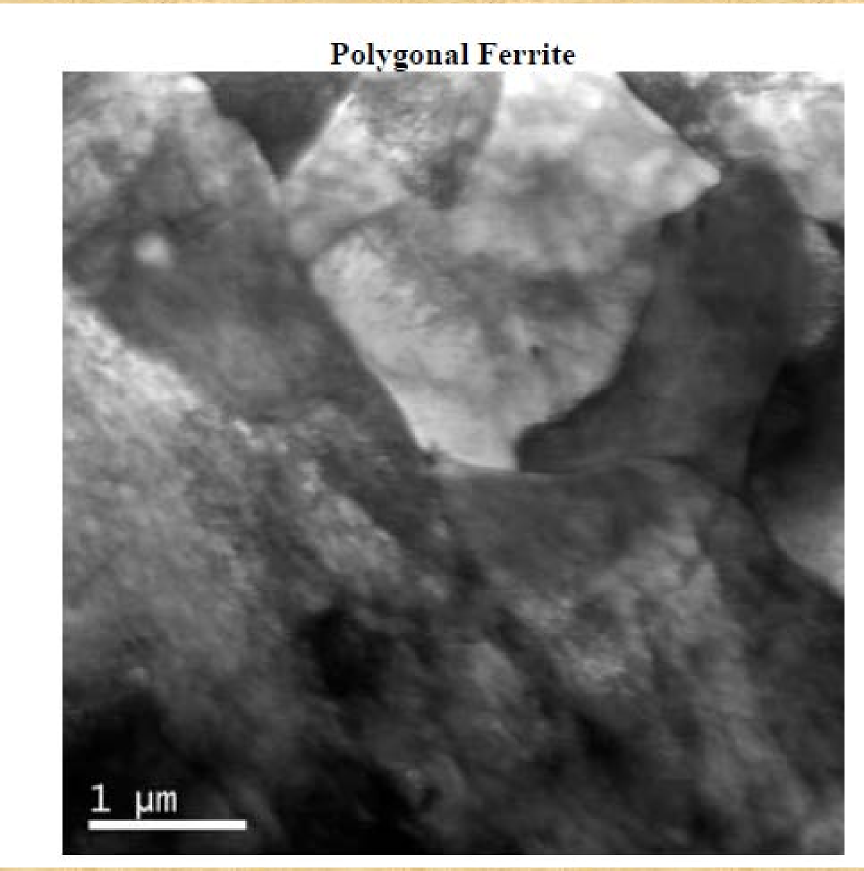
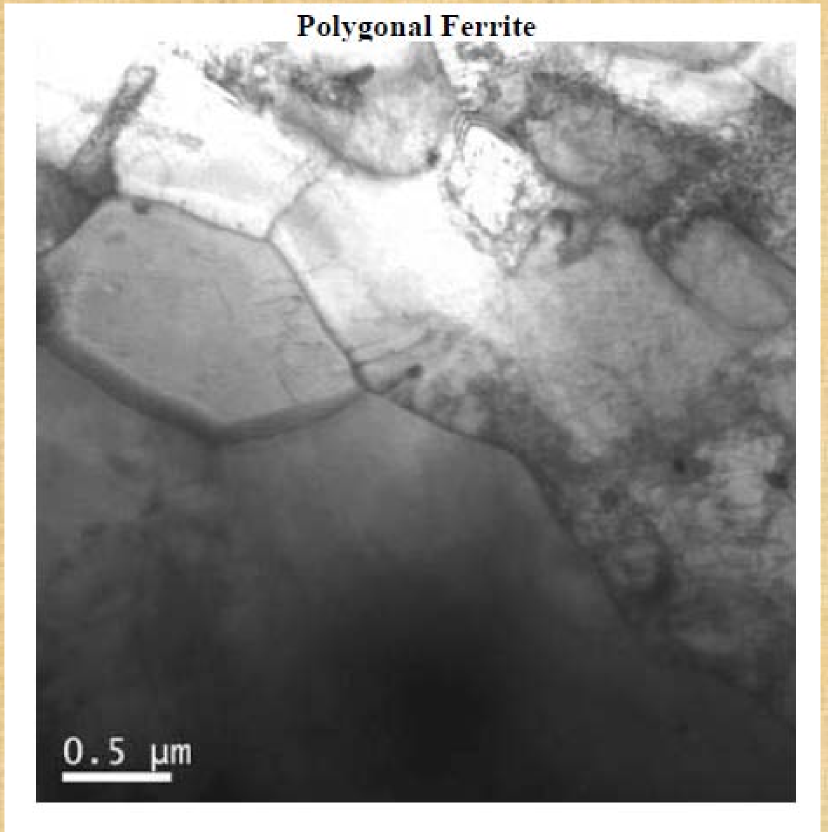
TEM Analysis





Approach - Additional Mechanical Property Characterization

- Alloy’s B and D’s performance across the range of pressures and strain rate in tensile testing appeared to achieve the best performance of the four tested alloys/microstructures.
- Alloy’s B and D were chosen to be further characterized for mechanical properties through fracture toughness and fatigue testing.
- Pressures of 800 and 3000 psi were chosen for the additional characterization work.
- Fracture and fatigue testing were conducted by Sandia National Laboratory.

Approach - Additional Mechanical Property Characterization - Sandia Scope of Work

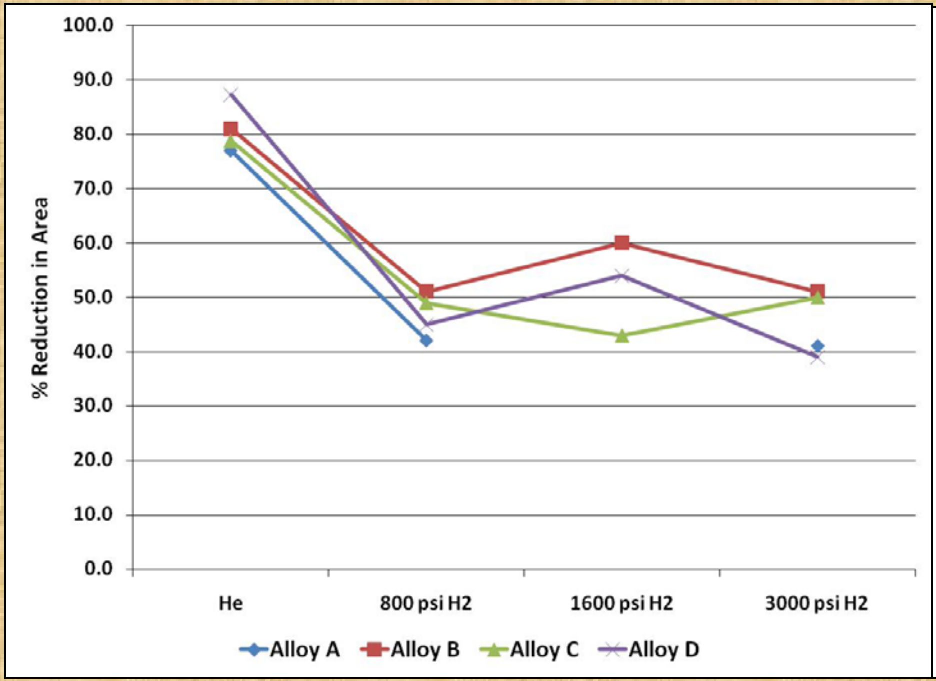
Test results consisting of replicate fracture toughness tests and replicate fatigue crack growth tests for two alloys at two hydrogen gas pressures. These results will include JR-curves (ASMT E1820) and fatigue crack growth curves (da/dn versus ΔK curves, ASTM E647).

Steel designation	Environment	# of fracture toughness tests	# of fatigue crack growth tests
Alloy B	800 psi H_2 gas	2	2
	3000 psi H_2 gas	2	2
Alloy D	800 psi H_2 gas	2	2
	3000 psi H_2 gas	2	2

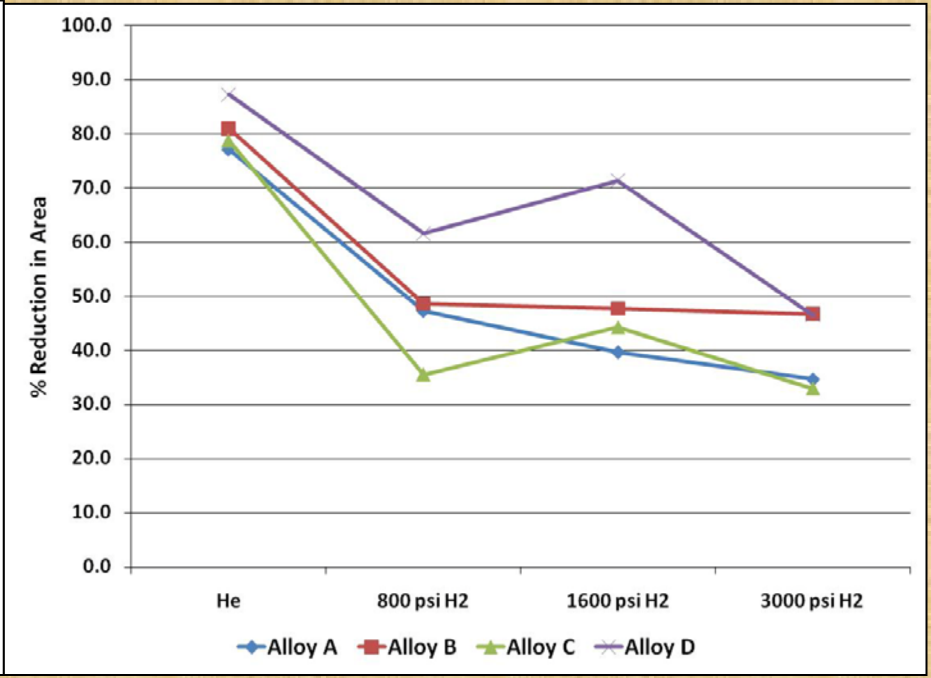
Note: For fatigue testing two R-ratios were evaluated – 0.5 and 0.1 (R is the ratio of the minimum to maximum load applied to the specimen).

Technical Accomplishments – *In-situ* Tensile Testing Results in Gaseous Helium and Hydrogen

Reduction in Area, 10^{-4}



Reduction in Area, 10^{-5}

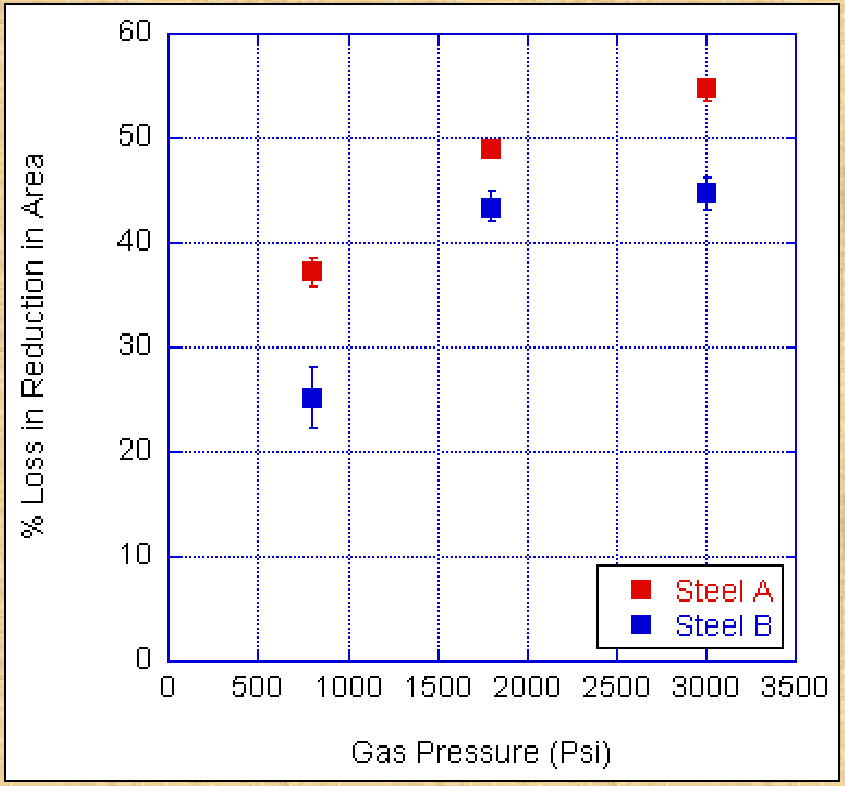


Technical Accomplishments - Additional Statistical Tensile Tests Performed on Steels A and B

% Loss in Reduction in area is defined as

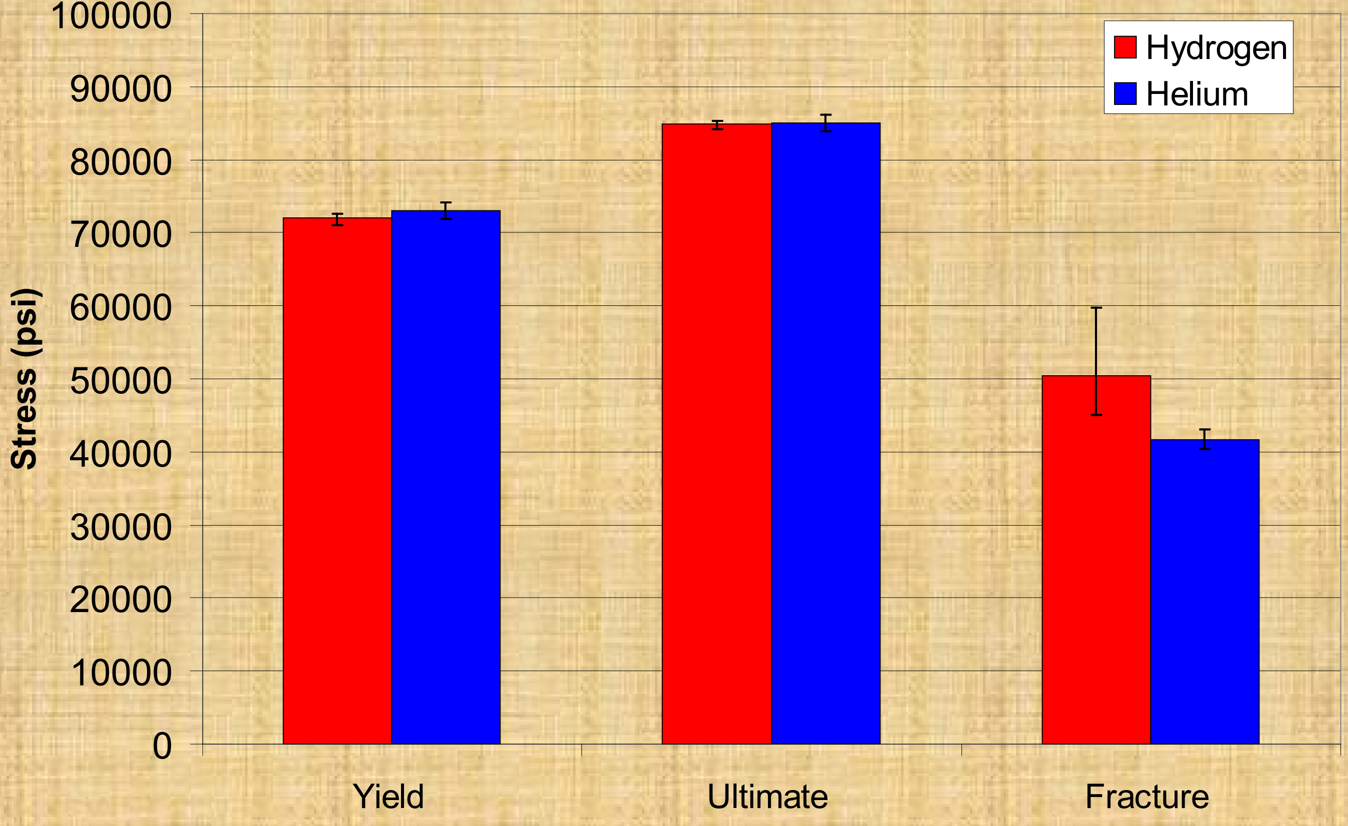
$$\left(\frac{\%RA(He)-\%RA(H_2)}{\%RA(He)}\right)*100$$

Observed % loss in RA is lower for Steel B at all pressures



•Pre-yield Strain rate = $1x10^{-5}$/sec

Technical Accomplishments - Yield and Ultimate Strength Alloy B Not Affected by Hydrogen



•Fracture stress is affected by the presence of hydrogen

Technical Accomplishments - Fracture Toughness Test Results – Alloy B and D, 800 psi

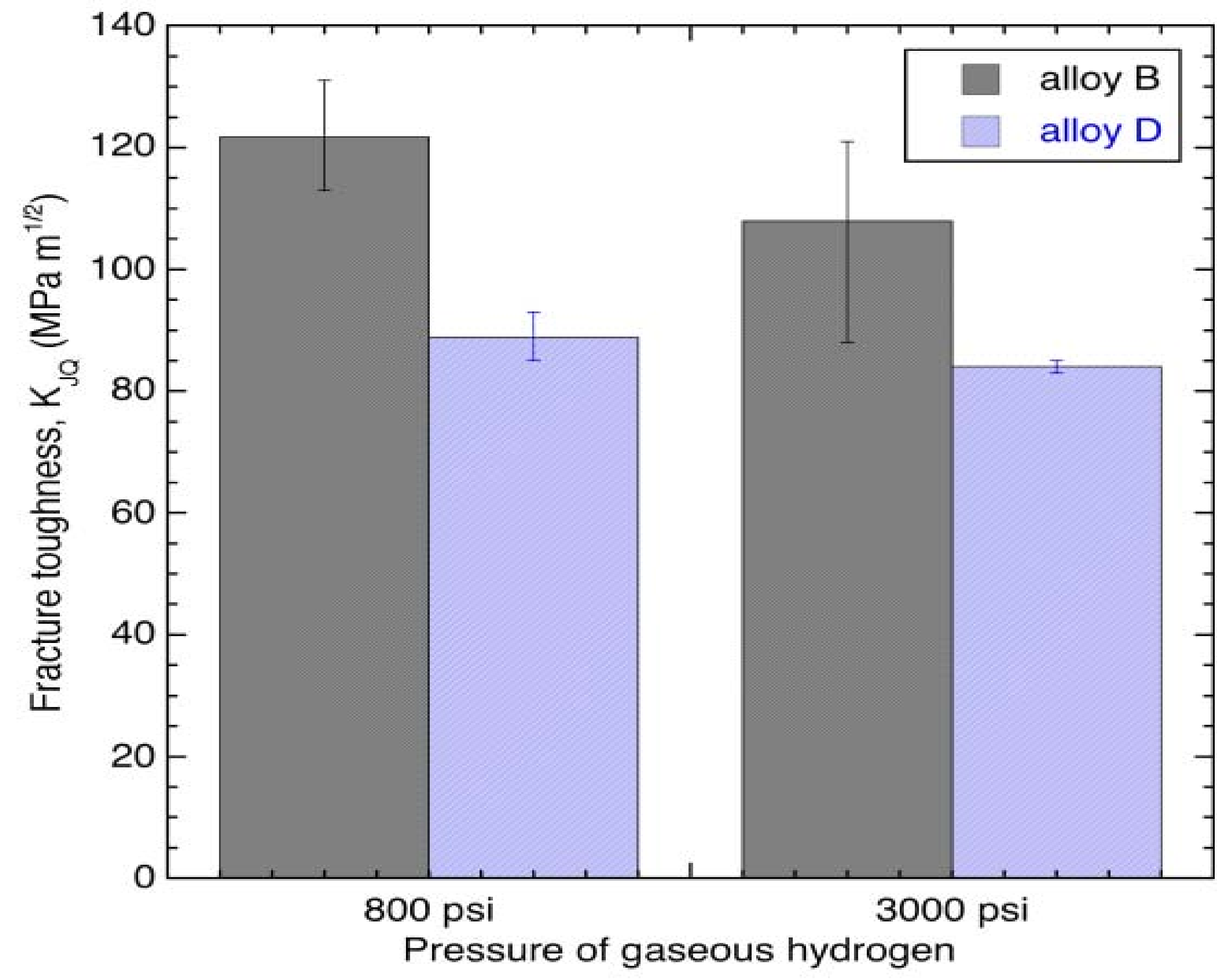
- **Alloy B**
  - Note separation in Alloy B23 fracture.
  - Maybe related to microstructural banding of chemically segregated centerline.
- **Alloy D**

Technical Accomplishments - Fracture Toughness Test Results – Alloy B and D, 3000 psi

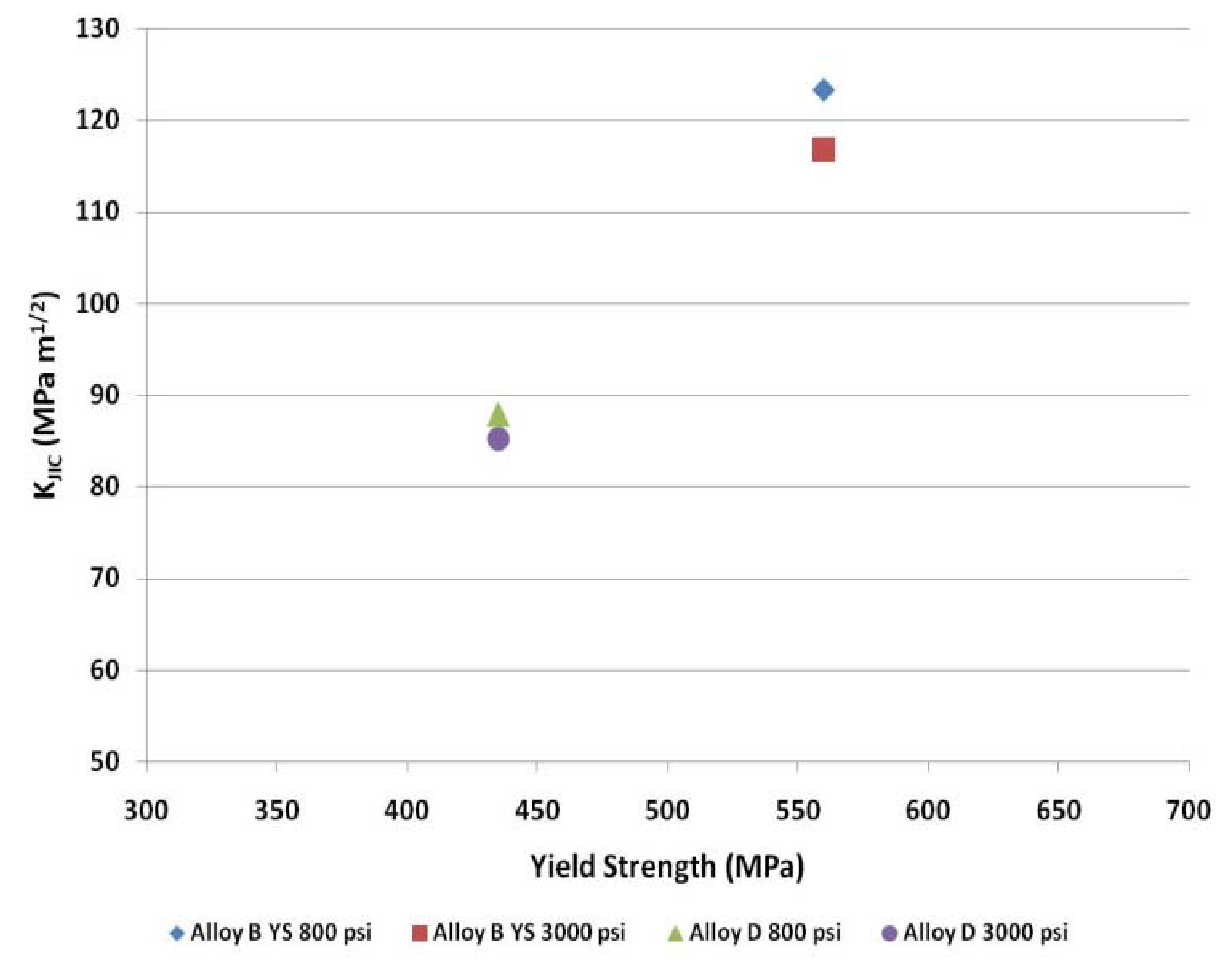
•Alloy B **•Alloy D**

•Note separation in Alloy B22 fracture. Maybe related to microstructural banding of chemically segregated centerline.

Technical Accomplishments - Fracture Toughness Test Results – Alloy's B and D, K_{JIC} vs. Pressure, Average Values

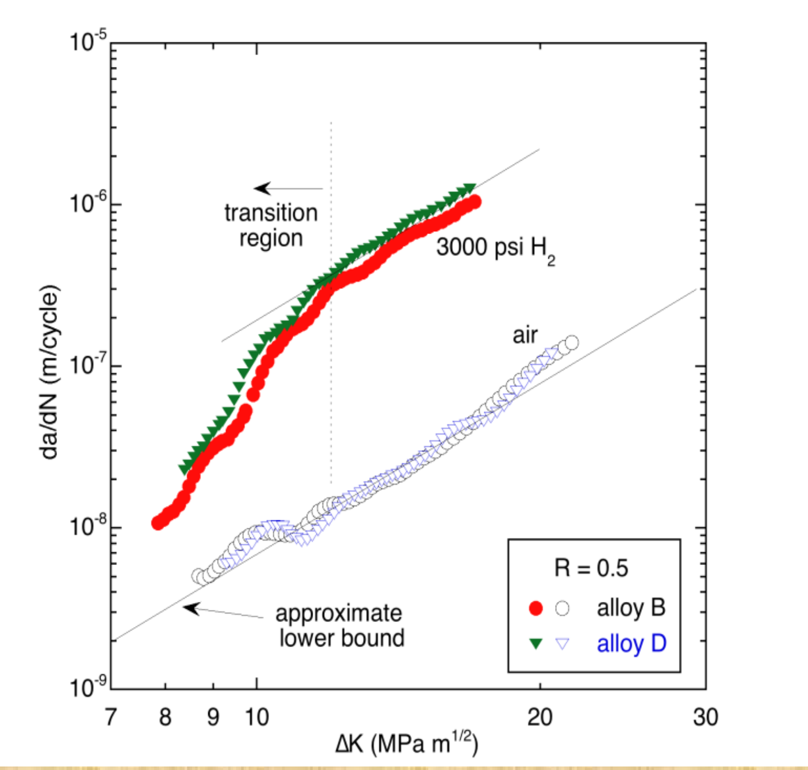


Technical Accomplishments - Fracture Toughness Test Results – Alloy's B and D, K_{JIC} vs. Actual Yield Strength, Average Values

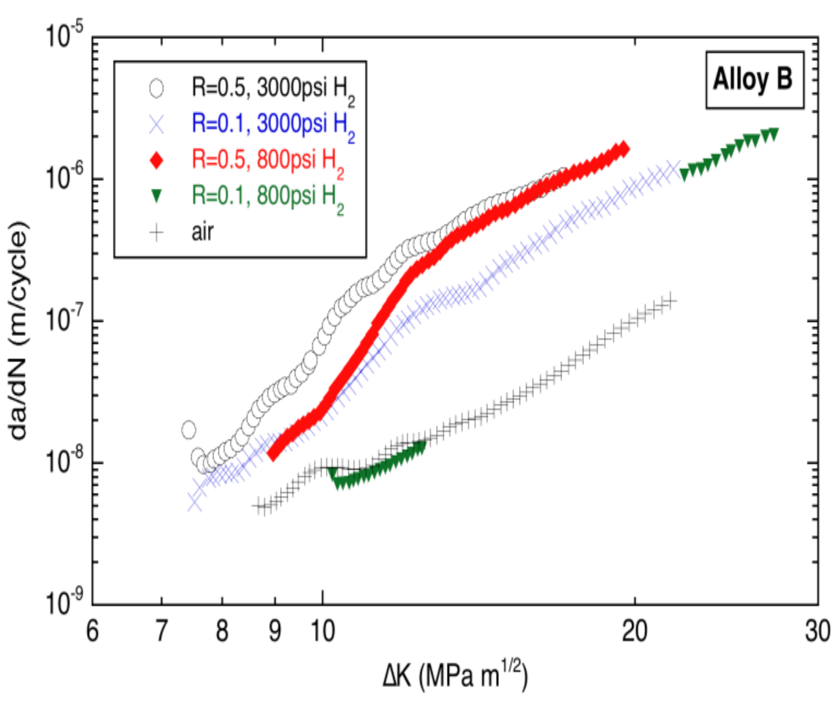


Technical Accomplishments - Fatigue Test Results – Alloy's B and D

FATIGUE CRACK GROWTH OF ALLOY B AND ALLOY D IN GASEOUS HYDROGEN AT PRESSURE OF 3000 PSI, COMPARED TO FATIGUE IN AIR



MEASURED FATIGUE CRACK GROWTH RATES FOR ALLOY B



Technical Accomplishments - Observations from Testing To Date

- Microstructure appears to play a role in resistance to the effect of H2.
  - Polygonal Ferrite/Coarse Acicular Ferrite (Alloy B) appears to be the best performer after tensile and fracture toughness testing, in fatigue testing both microstructures tested the fatigue crack growth rate (FCGR) were similar.
- Increasing yield strength ***does not*** appear to necessarily result in decreased fracture toughness due to the effect of hydrogen in the 800-3000 psi pressure range tested. Microstructure dependent. This may be different than what others have reported at higher pressures.
- R-ratio values of 0.1 and 0.5 performed similarly in the fatigue testing for the two microstructures tested.
- At relatively high ΔK (>12 MPa $m^{1/2}$) the FCGR is about 20 times greater than air, however at lower ΔK the FCGR starts to converge for both air and H_2.
- Understanding the transition between FCGR that are similar to air and those that are 20 times greater is important and necessary.

Technical Accomplishments - Observations from Testing To Date

- Increasing pressure appears to decrease resistance to hydrogen effect. There maybe a potential threshold pressure for a given microstructure.
- Effect of strain rate and hydrogen pressure is complex and maybe dependent on microstructure.
- Even though there are changes to the reduction in area and fracture toughness how much change is required to deem a microstructure not suitable for service?
- Even though the polygonal ferrite/coarse acicular ferrite microstructure appears to perform the best, does this mean that the other microstructures would not be suitable for service?
- What is the effect of the actual oxide surface layer that is produced in the production of steels? Will it improve the test results? To what magnitude?

Collaborations

- **Partners**
  - ORNL (Federal) provided *in-situ* tensile testing and evaluation of results in high pressure gaseous hydrogen.
  - Coatings partners (Industry) on hold at this time.
  - DGS Metallurgical Solutions (Industry) active as industry technical lead in analysis and interpretation of results.
  - Other industry partners offer expertise as needed on analysis of results along with supply of samples for testing.
- **Technology Transfer**
  - University of Illinois (Academic, DOE H2 project participant) has been given sample from this project for their embrittlement work. Information exchange has been valuable between the two projects
  - Reference Metal Company (Industry) has provided funding and analysis of microstructures.
  - ASME (Industry) has offered input related to needs of B31.12 codes and standards development.
  - Information shared with Sandia National Laboratory (Federal) on steel microstructures and expected performance in gaseous hydrogen environment.

Future Work FY10

- **Steels**
  - Testing and evaluation of Alloy’s E and F for service in high pressure hydrogen, subcontracted to Sandia National Laboratory
    - Fracture mechanics testing at 800 psi and 3000 psi
      - JR Curves per ASTM 1820
    - Fatigue crack growth testing at 800 psi and 3000 psi
      - da/dn curves vs. ΔK per ASTM 647
  - Final microstructural characterizations to determine volume fractions of pearlite, ferrite, bainite, etc. in alternative Alloy’s E and F. Coordinated through Reference Metals Company.
  - Continued detail analysis and recommendations from data generated in fracture and fatigue testing.
  - All 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.

Future Work (Pending Public and/or Private Funding)

- **Steels –** this project has become the initial stages of developing a broader understanding of the property-microstructure-environmental relationships for steels used in gaseous hydrogen pipelines. There has been much interest by industry and societal standards to expand the scope to include additional pipeline and pressure vessel steels and welds. Limited initial work (Item 1 and part of Item 2 on matrix next slide) has begun on a Phase 2 with private funding based on the interest level of industry and societal standards organizations.

By filling in the proposed matrix (next slide) of mechanical properties along with data currently or already generated in the past couple of years in the presence of H_2 up to 3000 psi, there will be a characterization/representation of the majority of alloy/microstructure designs used in pipeline steels (base metal) along with some pressure vessel steels currently in service dating to the 1960's along with potential future pipeline construction.

Future Work (Pending Public and/or Private Funding)

Item #	Grade	Loc	Microstructure	C	Test/Pressure
1	2000’s X70/X80 w Moly Design	Sandia	100% FAF	.05	Fracture-Fatigue/800&3000 psi
2	2000’s X70/X80 w/o Moly Design	Sandia	30% PF/70% FAF	.05	Fracture-Fatigue/800&3000 psi
3	Early 1990’s X70 Design	Sandia	85-90% PF/10-15% P	.08	Fracture-Fatigue/800&3000 psi
4	Late 1990’s X70 Design	Secat	92% PF/8% UB	.08	Fracture-Fatigue/800&3000 psi
4	1980’s X70 Alloy Design	KM?, other?	PF/P (10-20%),TBD	.11?	Fracture-Fatigue/800&3000 psi
5	1960’s X52 Alloy Design	KM	PF/P (30%+), TBD	.26	Fracture-Fatigue/800&3000 psi
6	1990’s/2000’s X52 Alloy Design	KM? AL?, Sandia?, other?	PF/P (10%) TBD	.10?	Fracture-Fatigue/800&3000 psi
7	ASTM A516 Gr70 w/o microalloy - PV	TBD	PF/P (40+%) TBD	0.23?	Fracture-Fatigue/800&3000 psi
8	ASTM A516 Gr70 w/o microalloy - PV	TBD	PF/P (40+%) TBD	0.23?	Fracture-Fatigue/800&3000 psi
9	X70 Pipeline Long Seam Welds	Secat	As-castTBD	?	Fracture-Fatigue/800&3000 psi
10	Pipeline Girth Welds	TBD	As-castTBD	?	Fracture-Fatigue/800&3000 psi

Project Summary

Relevance: Establish potential suitability of steel pipelines for gaseous hydrogen service.

Approach: Utilizing commercially available existing pipeline steels and industry expertise generate relevant mechanical property data vs. microstructure in the presence of high pressure gaseous hydrogen.

Technical Accomplishments and Progress: Demonstrated that two of four commercially available pipeline microstructures have potential to minimize hydrogen effect at pressure. Demonstrated that one of the final two performed better in fracture toughness testing. Fatigue testing using 2 different pressures and R-ratio values did not vary significantly between the two final microstructures tested. Microstructural characterization of 4 alloys completed.

Technology Transfer/Collaborations: Active participation with other DOE hydrogen research funded national laboratories and Universities along with utilization of available industry experts.

Proposed Future Research: Complete microstructure characterization of alternative microstructures. Complete fracture and fatigue testing of alternative microstructures at 2 pressures for comparison to existing pipeline steels. All data generated will be shared with ASME B31.12. Additional evaluation for suitability for service, additional testing of other pipeline microstructures, and economic analysis will be dependent on future public and private funding. Any additional information generated will be shared with ASME B31.12.