A Combined Materials Science/Mechanics Approach to the Study of Hydrogen Embrittlement of Pipeline Steels

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2011 DOE Hydrogen and Fuel Cells Program Review
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Project ID # PD023

Overview

Timeline

- Project start date: 5/1/05
- Project end date: 12/31/11
- Percent complete: 75%

Budget

- Total project funding: $1,500,000
- Share
  - DOE : 80% -- $1,200,000
  - Contractor : 20% -- $300,000
- Sponsor funding received
  - FY2010: $300,900
  - FY2011: $0K (Project under a no-cost extension)

Barriers

- **High Capital Cost and Hydrogen Embrittlement of Pipelines**
  - Determine suitable steels or other materials of construction to provide safe and reliable transport in pipelines while reducing the capital costs
  - Explore whether existing natural gas pipelines can be used to transport mixtures of natural gas and hydrogen without hydrogen embrittlement

Partners

- **Industrial**
  - SECAT
  - DGS Metallurgical Solutions, Inc.
  - Air Liquide
  - Air Products
  - Kinder Morgan
- **National Laboratories**
  - Sandia National Laboratories
  - Oak Ridge National Laboratory
- **Codes and Standards**
  - ASME
  - Japan Automotive Industry

Objectives - Relevance

- To come up with a *mechanistic understanding* of hydrogen embrittlement in pipeline steels in order to devise *fracture criteria* for safe and reliable pipeline operation under hydrogen pressures of at least 15MPa and loading conditions both static and cyclic (due to in-line compressors)
  - Study existing natural-gas network of pipeline steels (Kinder Morgan) or hydrogen pipelines (Air-Liquide, Air Products)
  - Working with Oregon Steel Mills (SECAT, DGS Metallurgical Solutions, Inc.) to propose steel microstructures with superior tolerance to hydrogen

- It is emphasized that such fracture criteria are lacking and there are no codes and standards for reliable and safe operation of pipelines in the presence of hydrogen
  - No engineering of pipelines based on the fundamental science underlying the effect of hydrogen on materials
  - Current design guidelines for pipelines only tacitly address subcritical cracking by applying arbitrary and conservative safety factors on the applied stress

- Illinois mechanism-based fundamental science approach
  - Will provide guidelines for the testing and design of pipelines for safe and reliable operation
  - Help avoid unnecessary repairs and shut-downs by minimizing unnecessary levels of conservatism in the operation of pipelines
  - Reduce capital cost by avoiding conservatism

Approach – Milestones

- Permeation experiments to identify diffusion characteristics
  - Collaboration with Oak Ridge National Laboratory
- Microstructural characterization
  - Materials from pipelines in service from Air-Liquide, Air-Products, and new steel microstructures from Oregon Steel Mills (SECAT, DGS Metallurgical Solutions, Inc.)
- High resolution scanning electron microscopy combined with topographical reconstruction of fracture surfaces along with transmission electron microscope analysis of samples extracted through focused ion beam machining
  - Relationship of microstructure and the fracture mechanism
- Developed finite element code to simulate transient, stress-driven hydrogen diffusion coupled with material elastoplastic deformation
  - Time to steady state in fracture process zone ahead of a crack tip is ~minutes
- Developed thermodynamic theory for the determination of the cohesive properties of particle/matrix interfaces and grain boundaries as affected by the presence of hydrogen solutes
  - Carried out *ab-initio* calculations of cohesive properties to understand the underlying fundamentals
- Simulated and identified deformation and constraint characteristics at an axial crack on the inner diameter (ID) surface
  - Laboratory specimen type (hydrostatic constraint guidelines) has been identified to investigate fracture conditions in a real-life pipeline

Milestones for 2010-2011

- Rising-load fracture testing performed at Sandia National Laboratories Fracture mechanism has been identified
  - Discovery of what quasi-cleavage is
- Ongoing fatigue testing
  - Hydrogen effects on fatigue crack growth rate
- Go/no-go decision on the hydrogen-induced change of interfacial cohesive energy
  - Developed a thermodynamic theory of decohesion (Dadfarnia *et al*. 2008, 2009) with parameter calibration through the use of *ab-initio* calculations.
  - Perform ed parametric studies on the hydrogen effect on cohesion reduction at second phase particles, e.g. MnS
- Ongoing work on development of fracture criterion based on hydrogen-induced void growth mechanism
  - Continuum and dislocation –based approach
  - Calculation of “Initiation Threshold”
- Our experiments so far indicate that pipeline steel types B and D are fairly resistant to hydrogen: Fracture toughness greater than 40MPa√m for pressures as high as 15 ksi.

MATERIALS

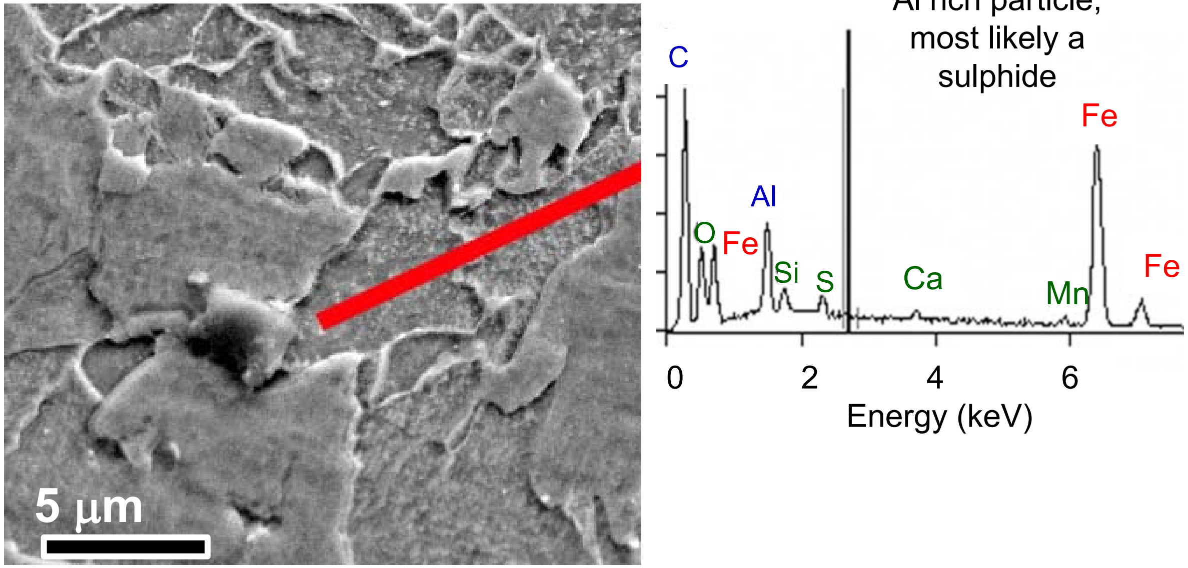
Steel B is a typical low carbon (0.05% by wt.) Mn-Si-single microalloy API/Grade X70/X80 capable of producing a ferrite/acicular microstructure. The alloy was found to perform well in sour natural gas service.

Steel D is a typical low carbon (0.03% by wt.) Mn-Si-single microalloy API/Grade X60, a predominantly ferrite microstructure with some pearlite. The alloy was found to perform very well in sour natural gas service.

Technical Accomplishment: Microstructural Characterization

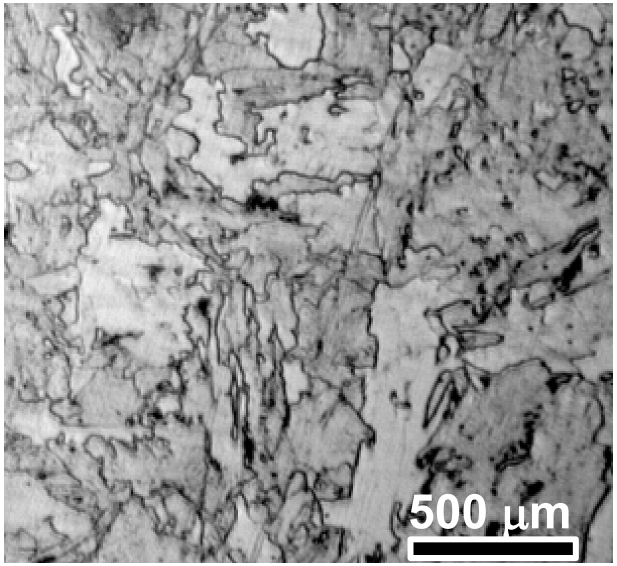
- Completed microstructural analysis of four “promising” pipeline steels provided by Oregon Steel Mills, and microstructures provided by Air-Liquide and Air Products
- Needed for hydrogen transport analysis

SEM analysis

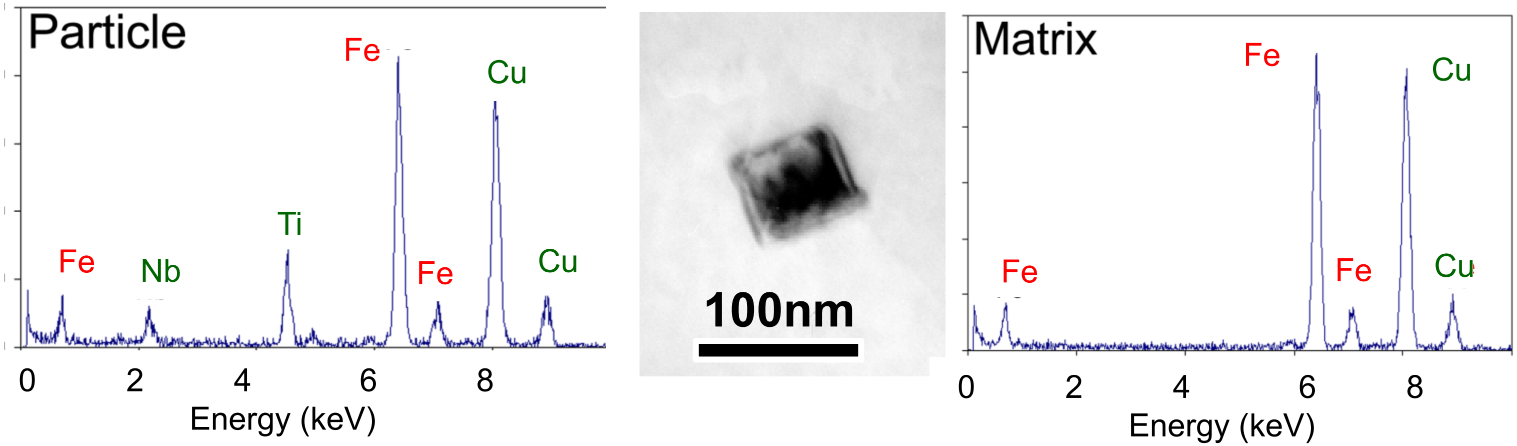


Al rich particle, most likely a sulphide

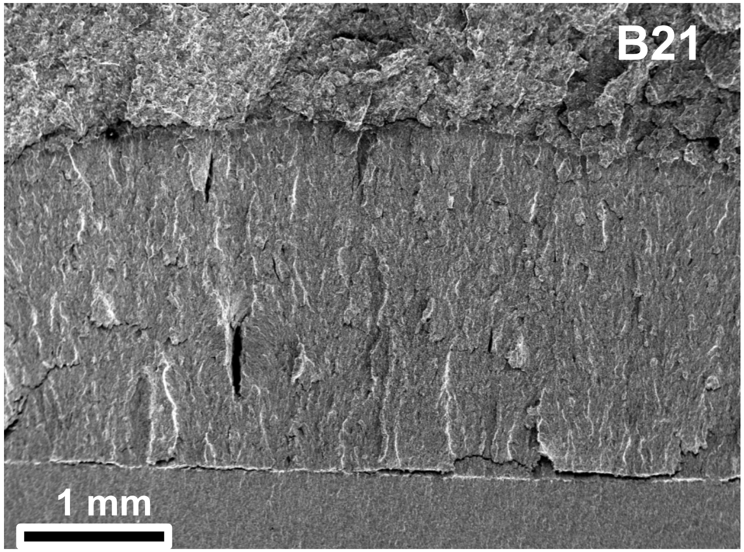
Optical microscopy



TEM image of a Ti, Nb particle

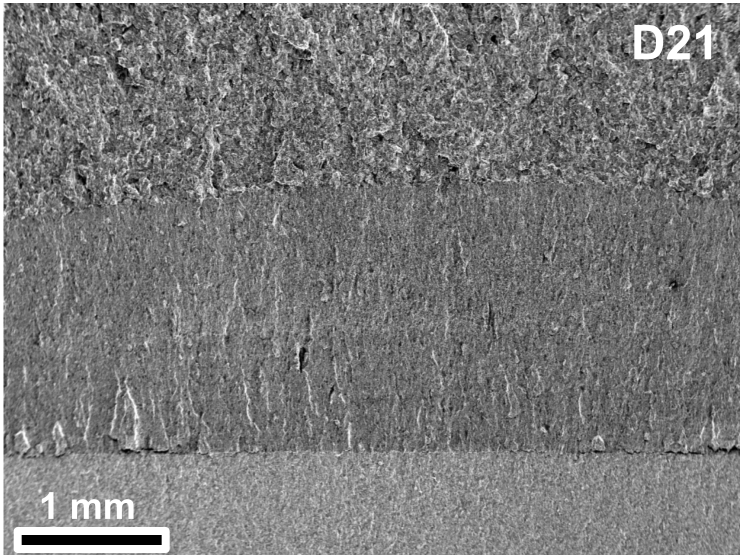


Technical Accomplishment: Wide-view SEM of New Pipeline Steel Microstructures B and D Fractured in 3 ksi H_2 gas



Images taken at Sandia

Hydrogen zone

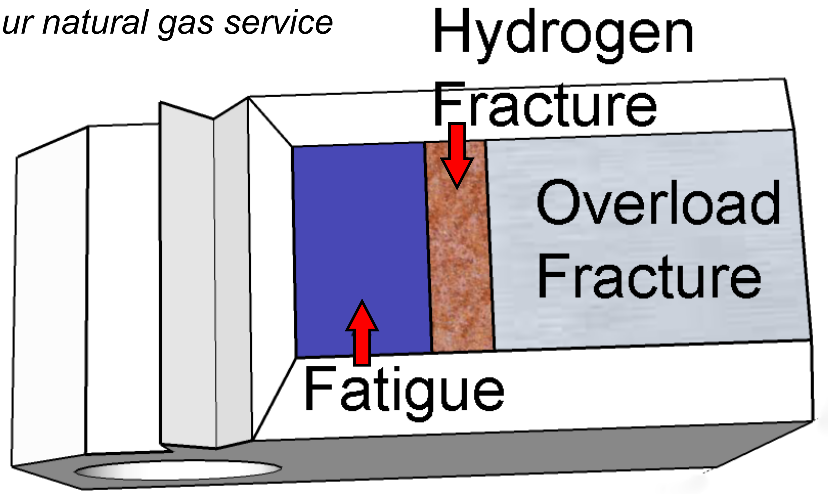


Steel B: low carbon (0.05% by wt.) Mn-Si-single microalloy API/Grade X70/X80 capable of producing a ferrite/acicular microstructure

Steel D: low carbon (0.03% by wt.) Mn-Si-single microalloy API/Grade X60, a predominantly ferrite microstructure with some pearlite

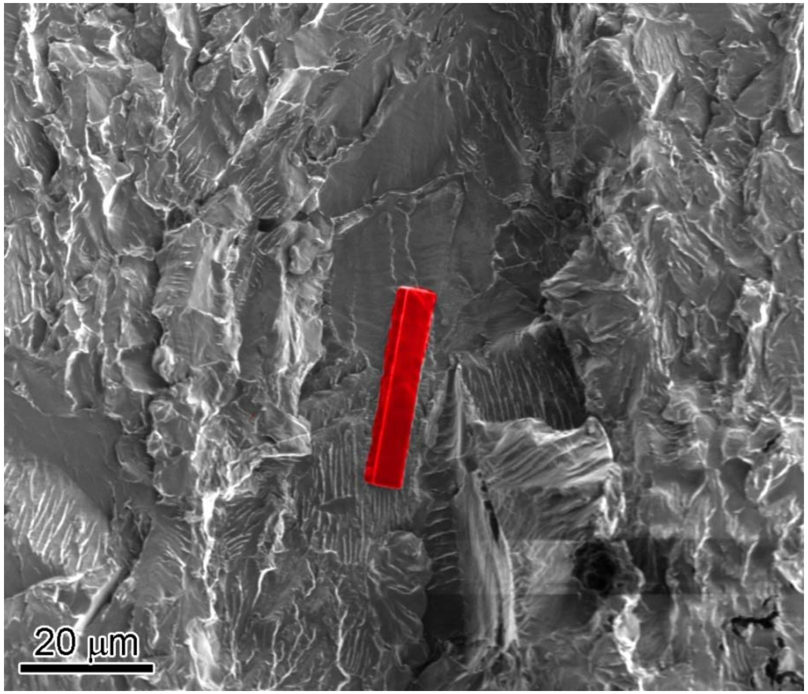
These alloys were found to perform very well in sour natural gas service

- Compact tension specimens tested in hydrogen environment at Sandia National Labs
- Area of fracture easily identified in SEM
- Identify features of interest



Technical Accomplishment: Hydrogen-Induced Fracture Surface Morphology – Quasi-Cleavage

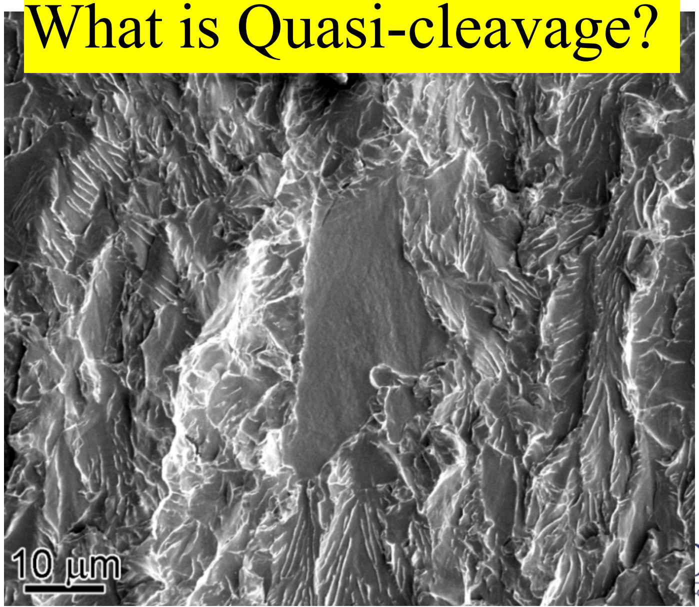
Feathery and featureless flat areas to extract Focused Ion Beam (FIB) samples



Closer view of two different morphologies


D21 steel fracture surface

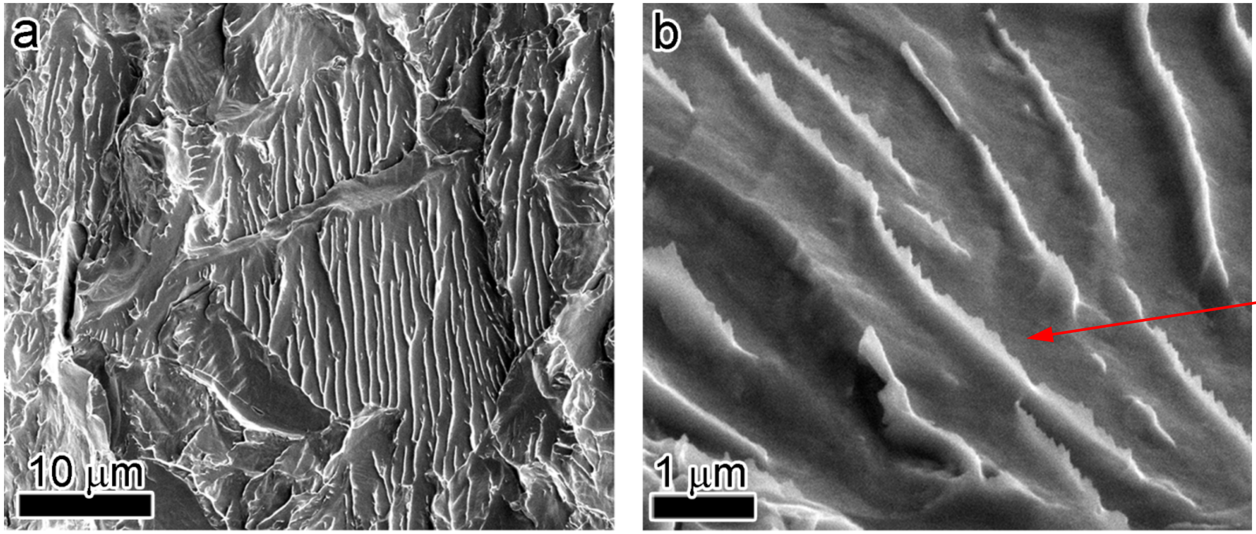
What is Quasi-cleavage?



Need to understand how these morphologies relate to microstructure and hydrogen effects on it.

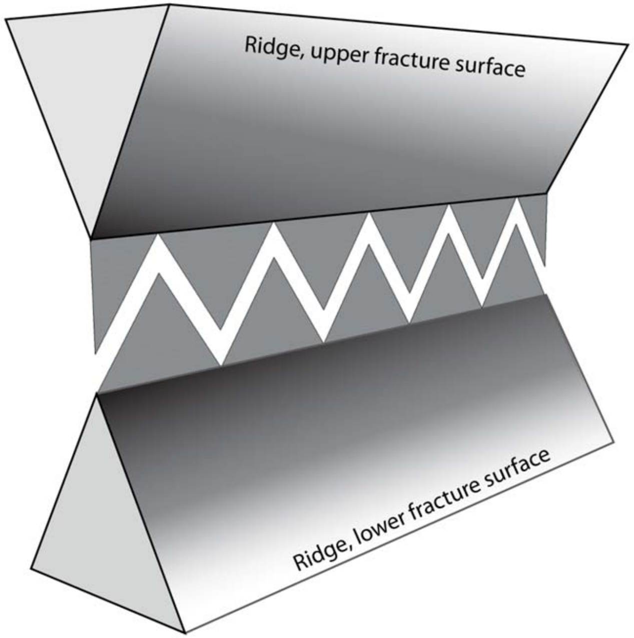
Two approaches used:
- high-resolution SEM + 3D visualization
- TEM images of material just beneath the fracture surface

Technical Accomplishment: Unique Features Identified on Fracture Surface



High-resolution SEM image reveals the presence of “saw-teeth” on top of the ridges. These are reminiscent of “saw-teeth” formed on final separation of thin sections in the transmission electron microscope.

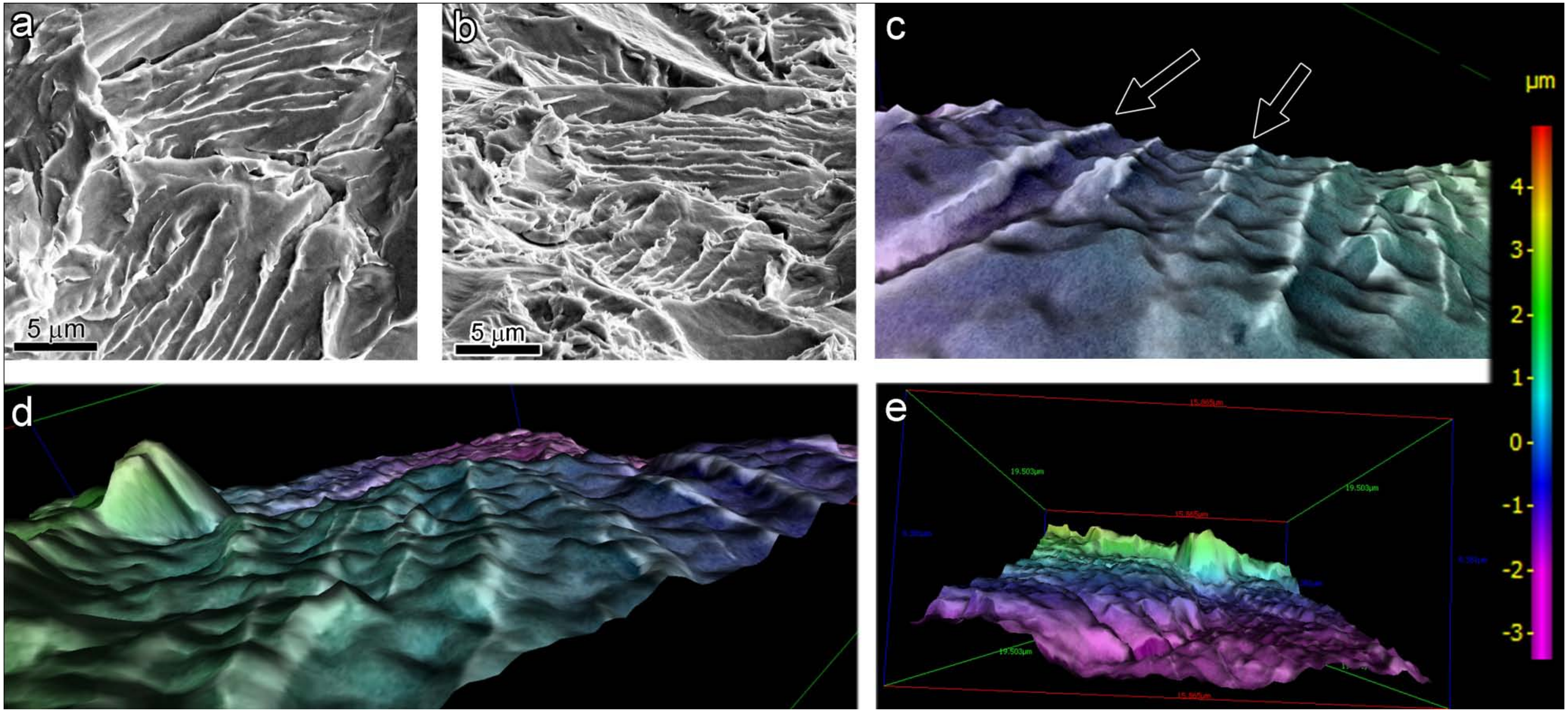
Final separation between ridges produces saw-teeth surfaces

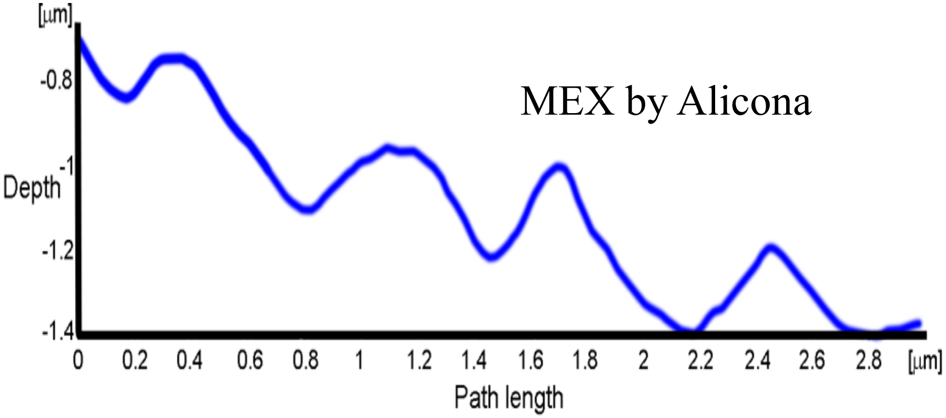


The mechanism of formation of the saw-teeth in the TEM sample is understood.

The presence of the ridges suggests plastic processes (final separation)

Technical Accomplishment: Ridge Surface Topography Confirmed by 3D Visualization

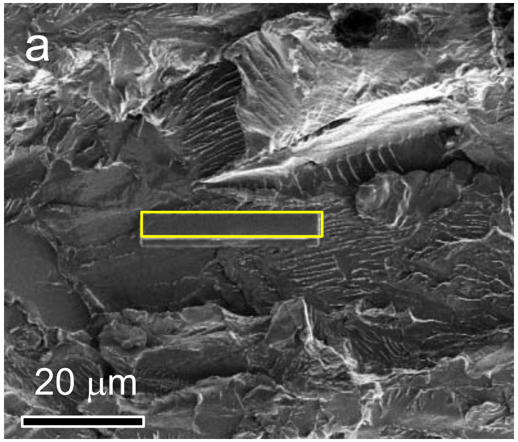




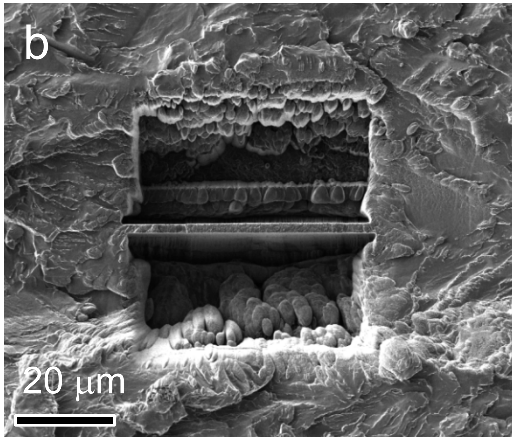
- 3-dimensional view reveals the surface topography confirming the ridge formation.
- Feature height measurement shows ridges are approximately protrusions of 200 nm.

Technical Accomplishment: Site Specific Sample Extraction From a Rough Surface Using Focused Ion Beam Machining

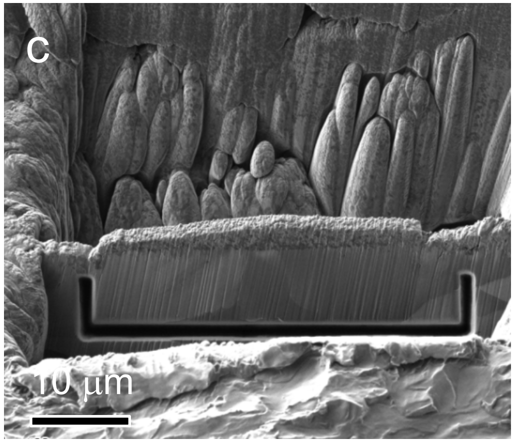
Select site, deposit Pt strip to identify and protect region

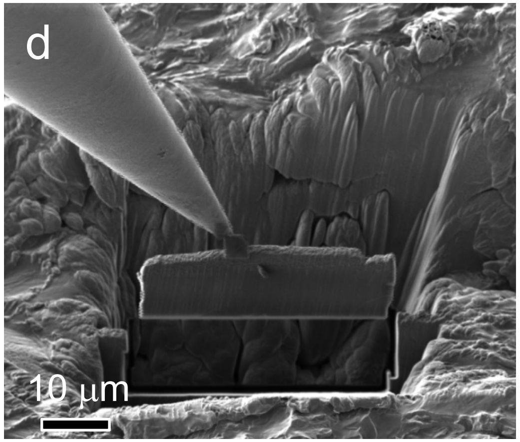


Machine out trenches on either side

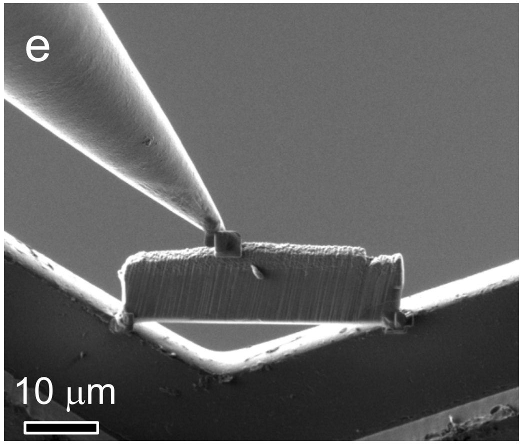


Make U-cut

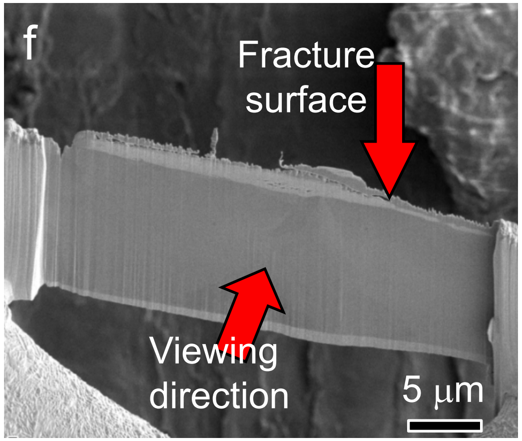




Attach needle to top of sample with Pt. Cut sample free by milling away remaining bridges and lift out



Attach sample to copper grid with Pt.



Cut needle free from sample thin to electron microscopy

Technical Accomplishment: Discovery of the Mechanism Responsible for "Quasi-Cleavage" Fracture

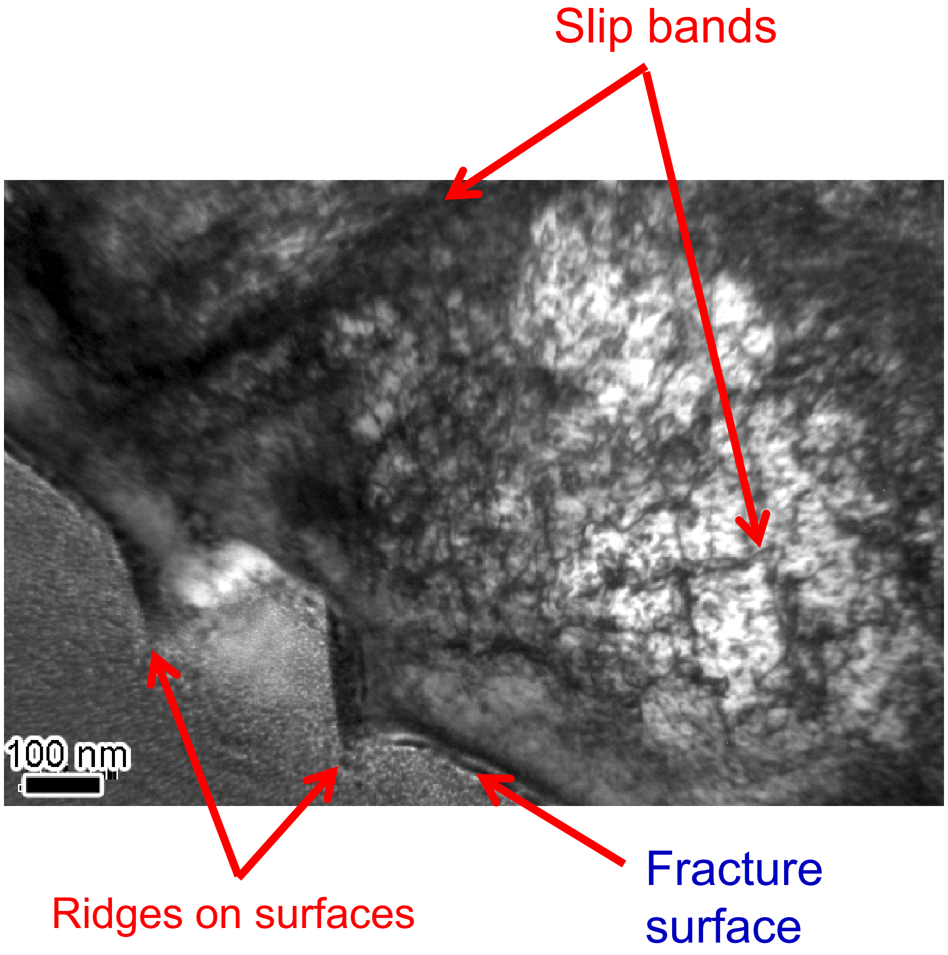
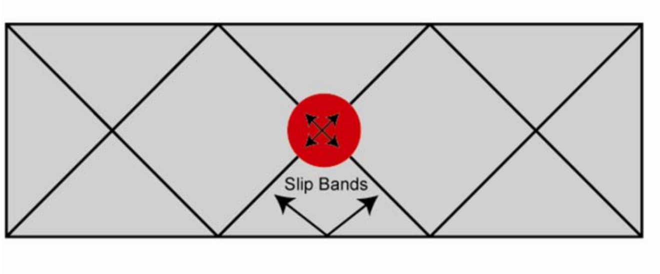


Image shows slip bands parallel to ridge edges, suggesting "*quasi-cleavage*" is not a cleavage like process but is related to dislocation slip. Enhanced and confined slip activity is consistent with hydrogen enhanced local plasticity (HELP) mechanism.

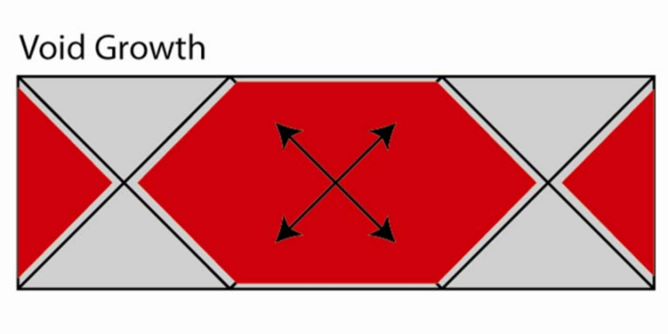
Guides development and introduction of new component in our model of the hydrogen-deformation interaction.

Slip planes densely packed with dislocations

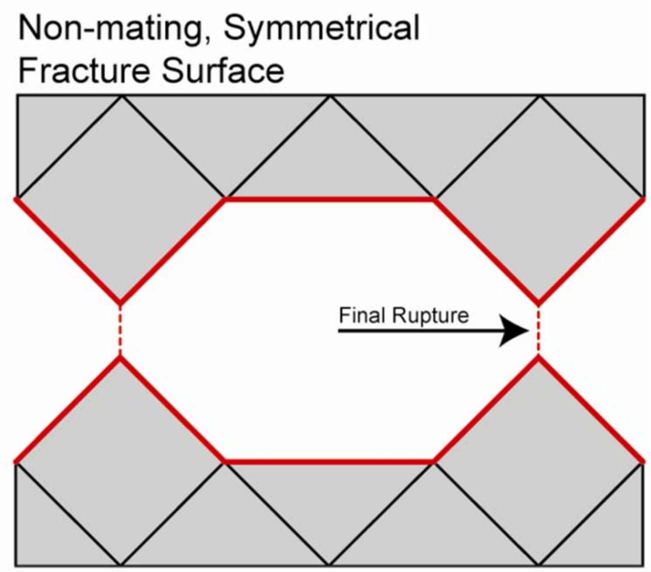
Technical Accomplishment: Hydrogen-Induced Quasi-Cleavage Fracture Explained



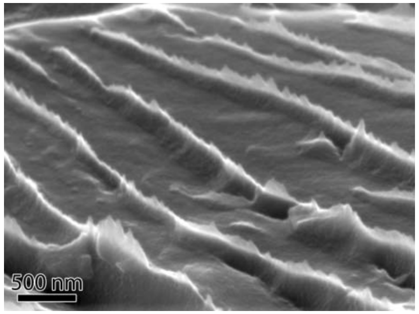
a) Hydrogen-induced void nucleation and growth at slip band intersections
   - Open along lines of intersection forming tubes



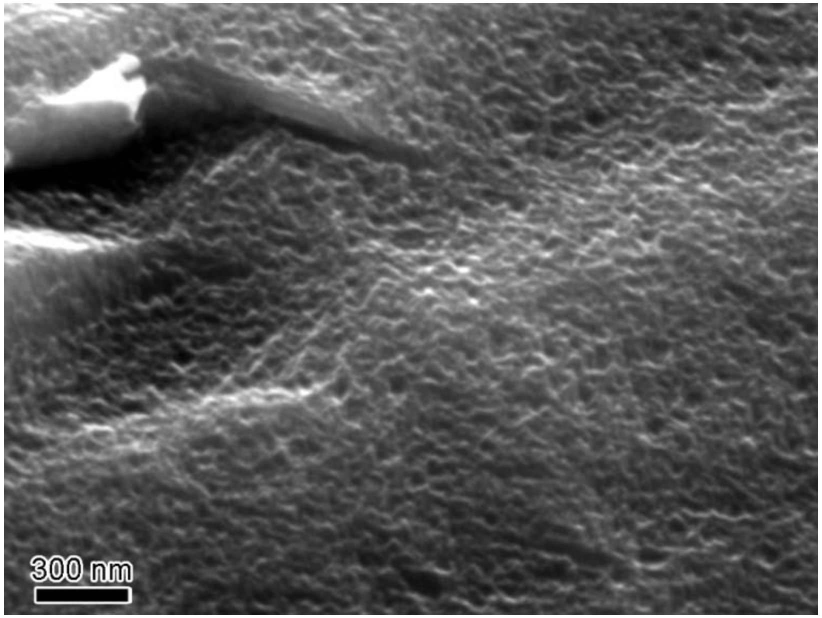
b) Voids expand by dislocation processes until they encounter another void

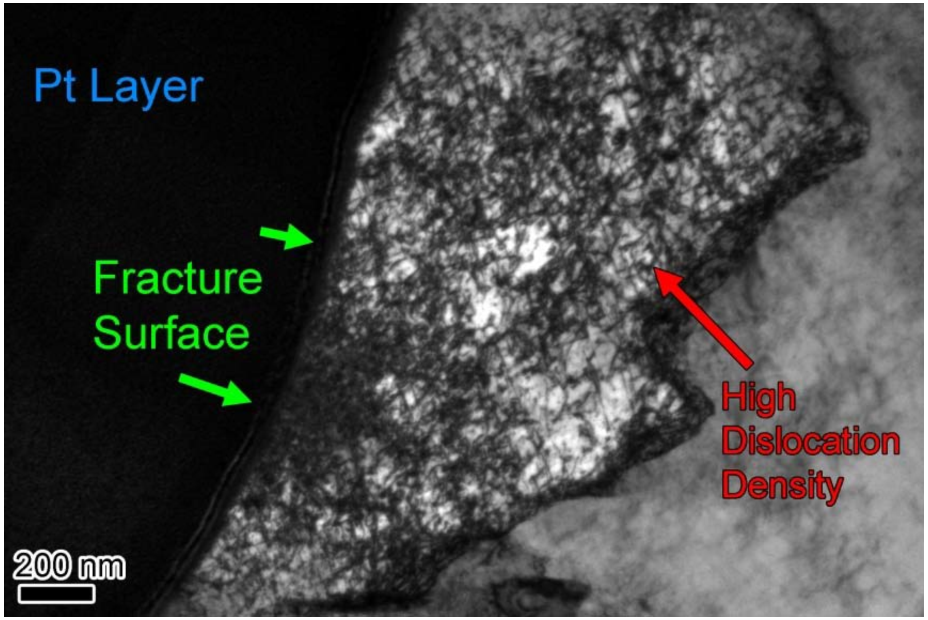


c) Final failure along tops of ridges forming saw-teeth



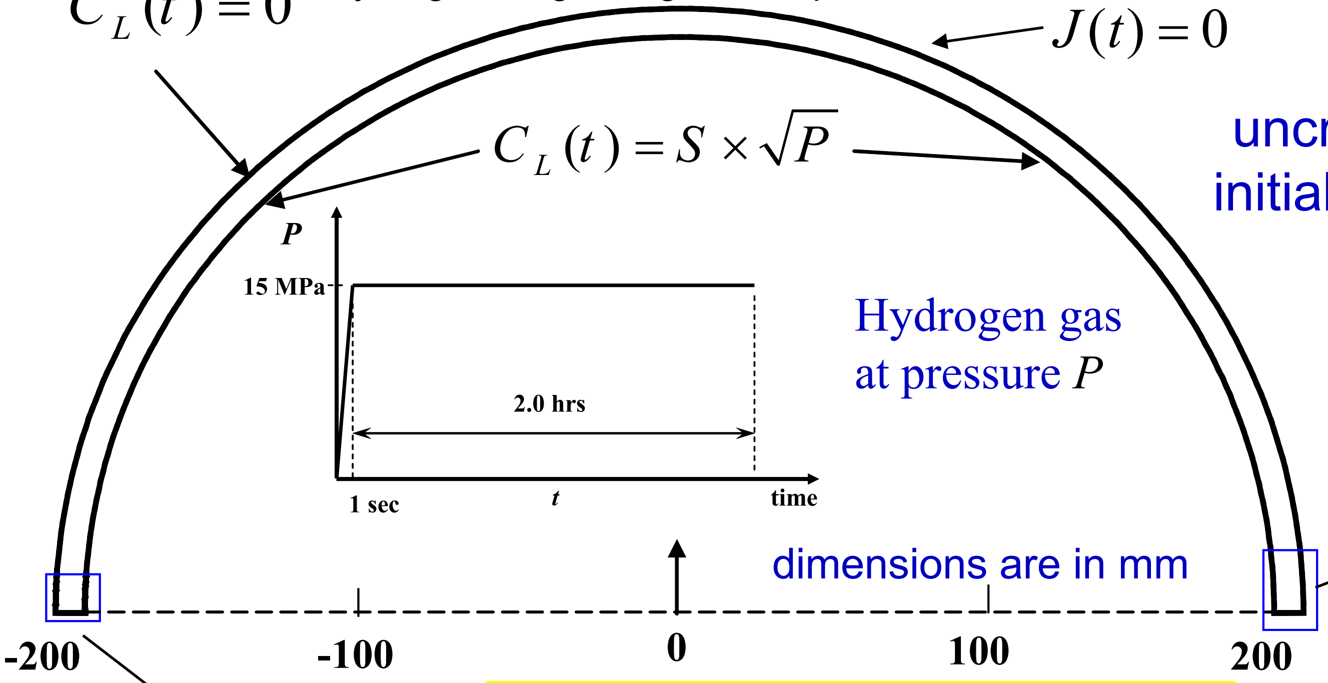
Technical Accomplishment: Discovery of the Mechanism Responsible for “Quasi-Cleavage” Fracture





- **What we see as flat surface in actuality is heavily dimpled!**
- **Fracture process is clearly ductile**
- **We are resolving these features**

Technical Accomplishment: Analysis of Cracked Pipeline



$C_L(t)=0$

Hydrogen outgassing or impermeable OD surface

$J(t)=0$

$C_L(t)=S\times\sqrt{P}$

Hydrogen gas at pressure P

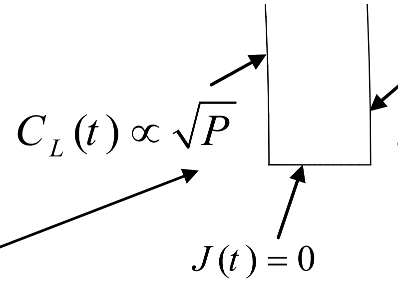
dimensions are in mm

outer radius: 8”

thickness: 0.375”

uncracked ligament: 0.356”

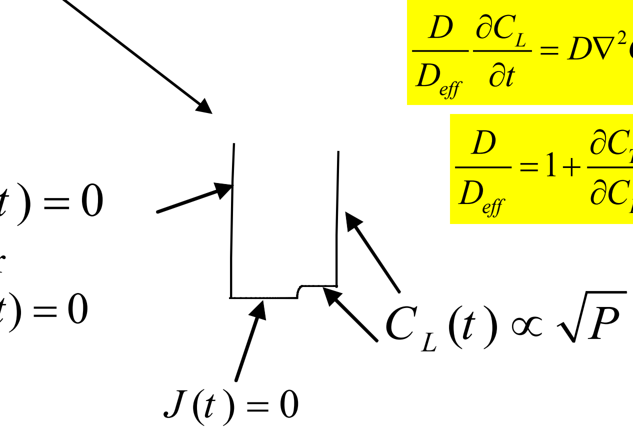
initial crack opening: 0.3 μm



$C_L(t)\propto\sqrt{P}$

$C_L(t)=0$
or
$J(t)=0$

$J(t)=0$



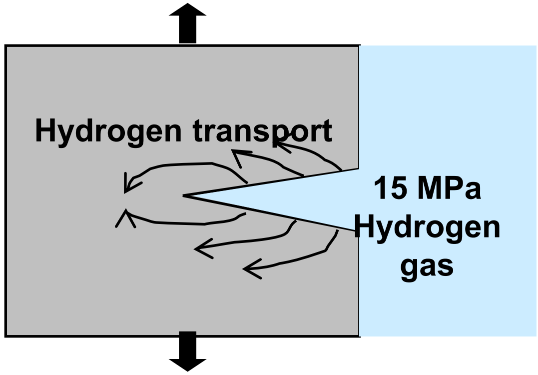
$C_L(t)=0$
or
$J(t)=0$

$C_L(t)\propto\sqrt{P}$

$J(t)=0$

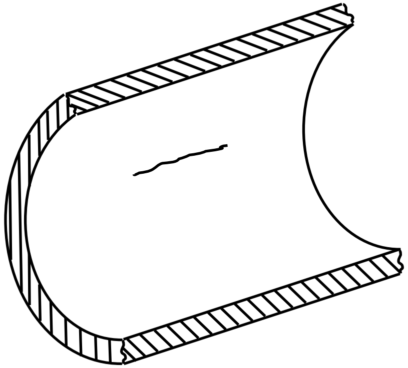
$$\frac{D}{D_{eff}}\frac{\partial C_L}{\partial t}=D\nabla^2 C_L-\nabla.\left(\frac{DC_LV_H}{3RT}\nabla\sigma_{kk}\right)-\alpha\theta_T\frac{\partial N_T}{\partial\varepsilon^p}\frac{d\varepsilon^p}{dt}$$

$$\frac{D}{D_{eff}}=1+\frac{\partial C_T}{\partial C_L}$$



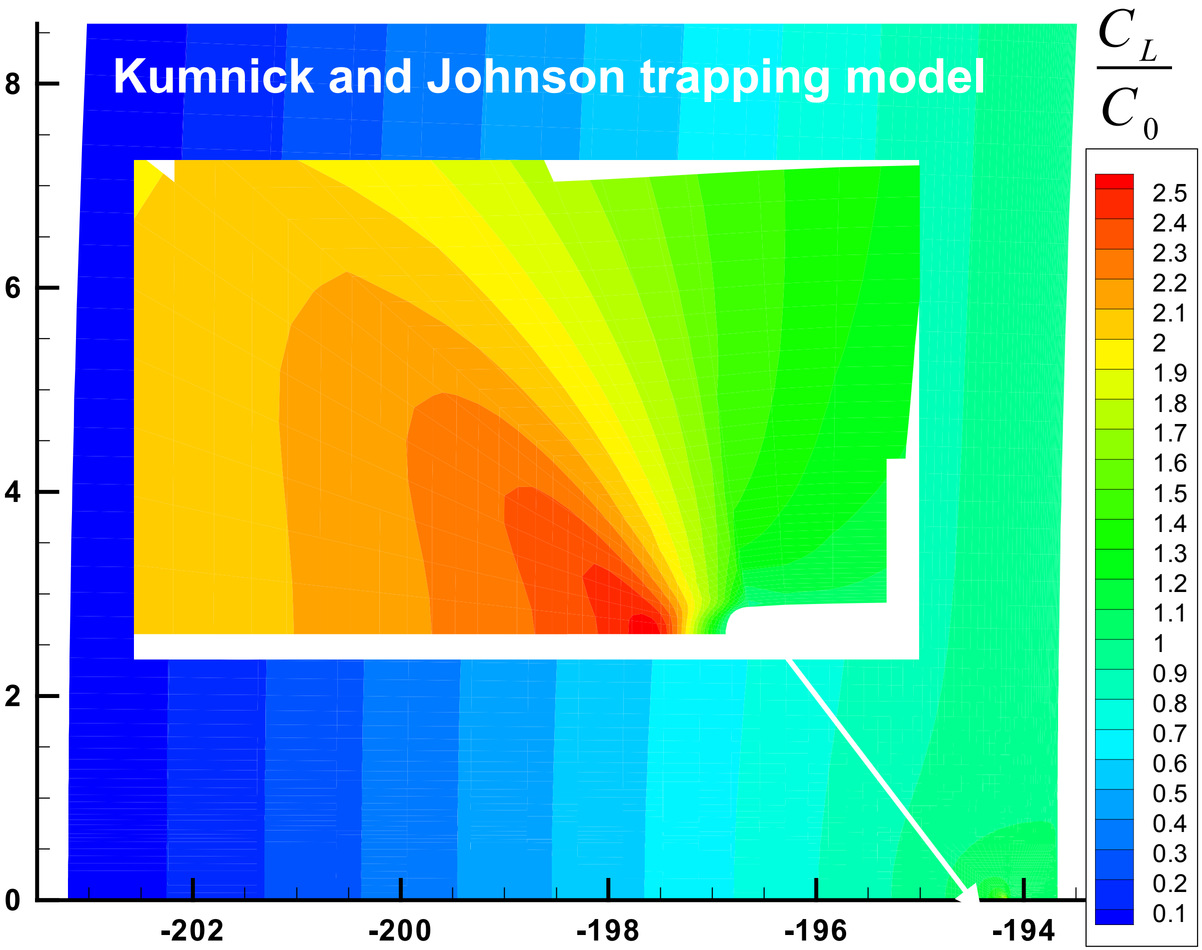
Hydrogen transport

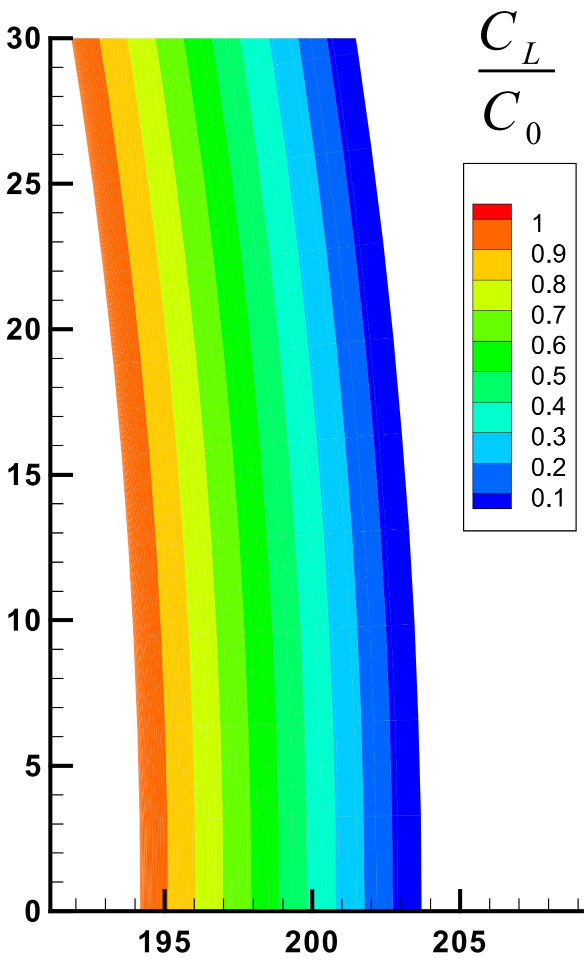
15 MPa Hydrogen gas



Technical Accomplishment: Hydrogen Concentration at Steady-State

Time to steady-state: 2.0 hr





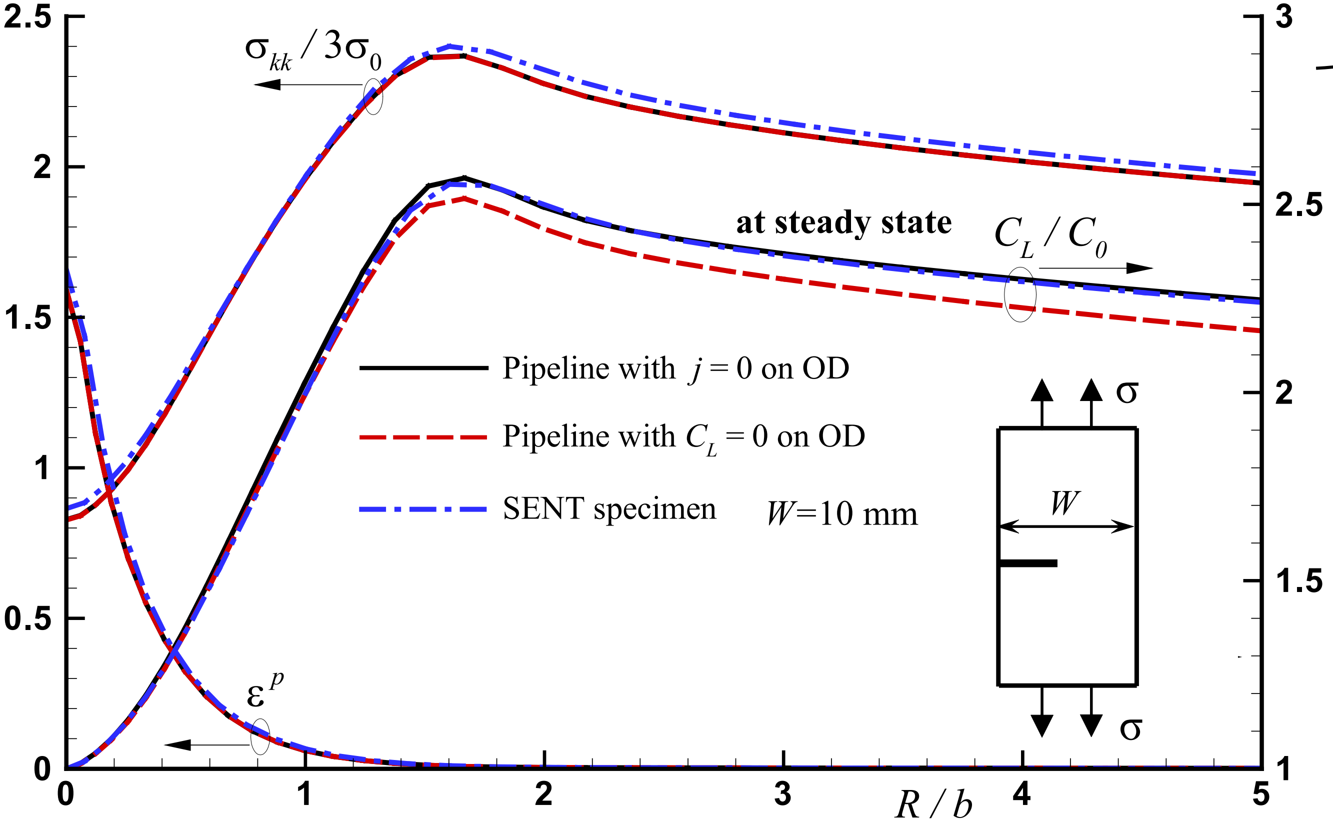
$$C_0 = 2.65932 \times 10^{22} \text{ H atom} / \text{m}^3$$

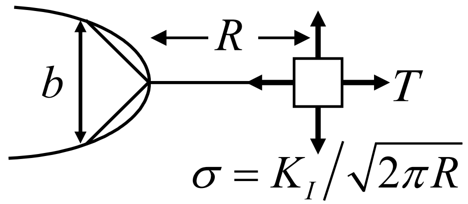
corresponds to lattice concentration at

$$P = 15 \text{ MPa}$$

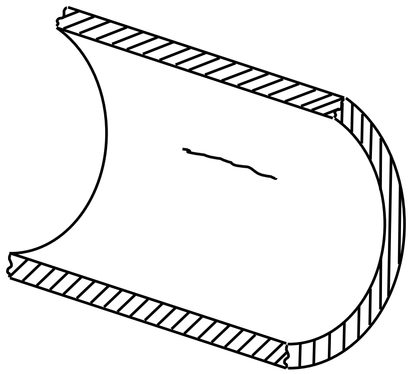
Technical Accomplishment: Environmental Similitude with Single Edge Notch Tension Specimen

Constraint fracture mechanics



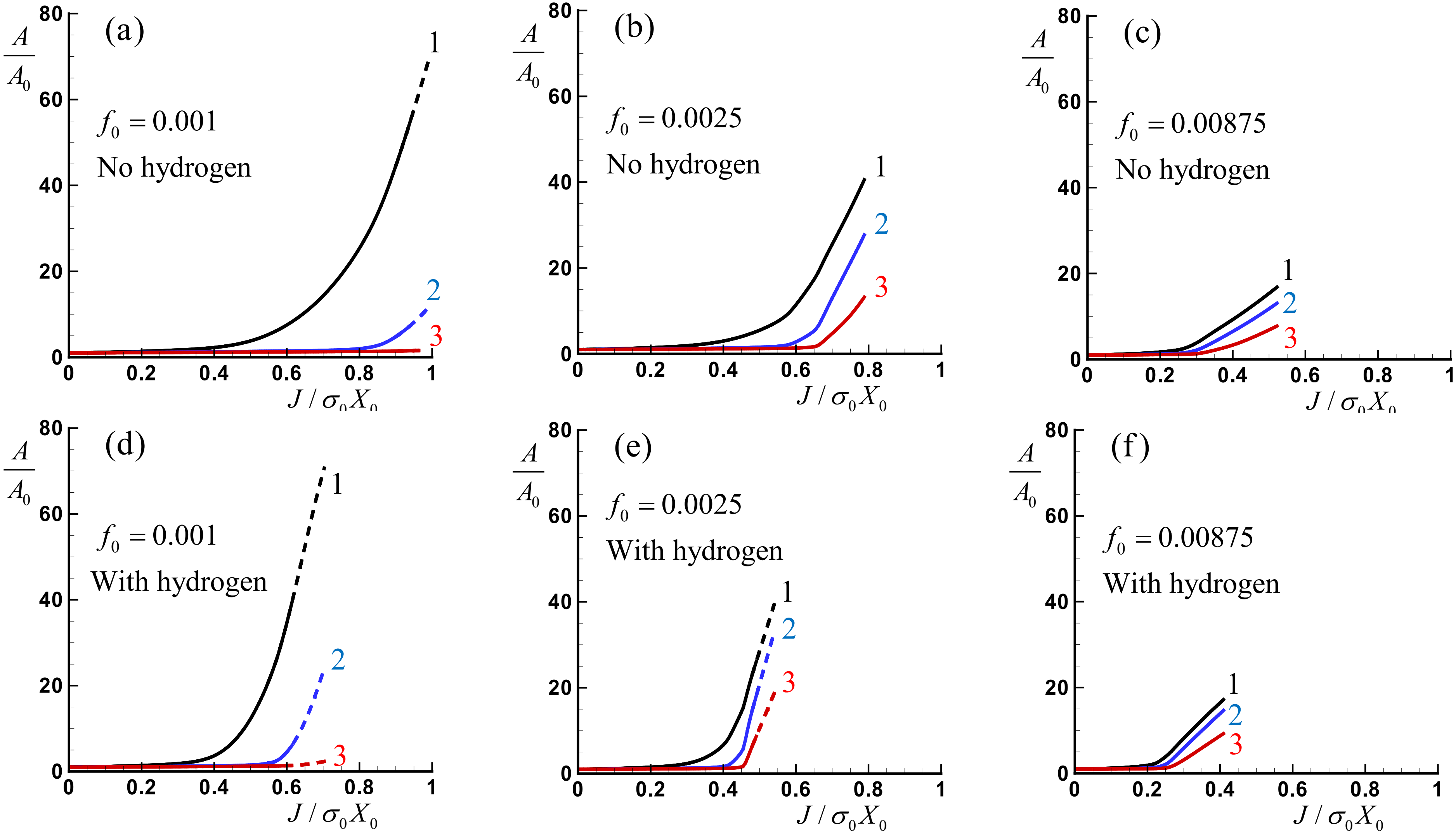


Cracked-Pipeline Fields vs. SENT-Specimen Fields

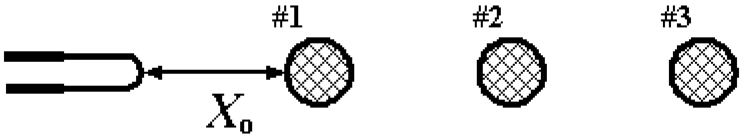


- Pipeline fields scale with the stress intensity factor and *T*-stress at the axial crack.
- Single Edge Notch Tension (SENT) specimens can be used to study fracture resistance of a pipeline with an axial crack

Technical Accomplishment: Void Growth at Various Initial Undeformed Volume Fractions



H Increases void growth rate and reduces fracture toughness



Technical Accomplishment: Hydrogen Effect on Fracture Toughness of Pipeline Steels

f_0	$J_{IC} / \sigma_0 X_0$			K_{IC} [MPa$\sqrt{\text{m}}$]	
	No hydrogen	**hydrogen**	**Reduction of fracture toughness**	**No hydrogen**	**hydrogen**
0.0010	0.988	0.703	29%	114.2	96.3
0.0025	0.790	0.540	32%	102.1	84.4
0.00875	0.524	0.410	22%	83.17	73.6

J_{IC} : Fracture toughness measured in terms of the *J*-Integral

f_0 : Void volume fracture (undeformed stage)

σ_0 : Yield strength

X_0 : Distance between voids

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Collaborations

Industrial Partners

- **SECAT, DGS Metallurgical Solutions, Inc., Oregon Steel MIlls**
  - Collaboration on new steel microstructures. Microstructural analysis includes Transmission/Scanning Electron Microscopy, Optical Microscopy, Energy Dispersive Spectroscopy, etc.
- **Air Liquide, Air Products**
  - Collaboration on microstructural analysis and testing of coupons from hydrogen pipelines in service
- **Kinder Morgan**
  - Natural gas pipeline in the presence of hydrogen (microstructural analysis and hydrogen uptake)
- **ExxonMobil Corporation**
  - Collaboration on the effect of microstructure on hydrogen embrittlement

National Laboratories

- **Sandia National Laboratories, Livermore**
  - Collaboration on all aspects of hydrogen embrittlement: fundamentals, experiments, and simulation. Collaboration includes summer visits by students and the PIs to the Laboratory at Livermore.
- **Los Alamos National Laboratory**
  - Collaboration on issues of fracture similitude between laboratory specimens and real-file components for gas transfer systems.
- **Oak Ridge National Laboratory**
  - Collaboration on hydrogen permeation measurements

Collaborations

- **ASME Codes and Standards**
  - Collaboration on safety factor calculations for hydrogen pipelines
- **International Collaborations (Japan)**
  - International Institute for Carbon-Neutral Energy Research (I^{2}CNER) at Kyushu University with satellite Institute at the University of Illinois
    - Collaborative research agreement between Kyushu and Illinois was signed on March 15, 2011
    - Collaboration on all aspects of embrittllement (e.g., fundamentals, microstructural analysis, experiments, simulations)
  - Institute for Hydrogen Industrial Use and Storage (HYDROGENIUS) at Kyushu University
  - Annual meetings with HYDROGENIUS and the Automobile Industry of Japan (Toyota, Honda, Nissan) on Hydrogen Technology Standards

Future Work

Experiment

- Identify the nature of the fatigue crack growth mechanism in the presence of hydrogen
- Characterization of the fracture-surface/underlying-microstructure relationship through TEM of FIB extracted samples

Modeling and Simulation

- Finish integration between modeling and simulation with experiment
  - Associate the fracture mechanism at the microscale with valid macroscopic indices of embrittlement such as critical stress intensity factor (Initiation threshold)
- Use modeling to guide experiments with regard to the parameter space
  - Similitude (mechanical and environmental)
  - Pressure course (frequency, wave, etc.)

Fatigue testing and modeling for damage tolerance assessment under cyclic pressure conditions

- Damage tolerance assessment: for a given hydrogen pressure and pipeline dimensions determine tolerable crack size for safe operation

$$da / dN \text{ vs. } \Delta K$$

Summary

- **Relevance**
  - Identify the mechanisms of hydrogen embrittlement of pipeline steels and propose fracture criteria with predictive capabilities to help development of codes and standards
  - Results indicate that new steel microstructures are hydrogen resistant
- **Accomplishments and Progress**
  - Microrstructural characterization and analysis (TEM, SEM, Optical) of pipeline steels (industrial and laboratory) has been completed
  - Discovery of the nature of the quasi-cleavage mechanism
    - identification of hydrogen-induced fracture mechanisms through FIB/TEM
  - Finite element codes of hydrogen transport interaction with material microstructure developed and tested
    - Unique simulation capabilities of the hydrogen effect on mechanical properties
    - Simulation of fracture initiation and crack growth tests
  - Association of the fracture mechanism at the microscale with valid macroscopic indices of embrittlement such as critical stress intensity factor (Initiation threshold)
- **Collaborations**
  - Active partnership with Sandia National Laboratories, Los Alamos National Laboratory, ASME codes and Standards, JAPAN (International Institute for carbon-Neutral Energy Research, Hydrogenius Institute), Industrial Partners (e.g. ExxonMobil, SECAT)
- **Proposed future research**
  - Damage tolerance assessment (safe operation of a cracked pipeline under given pressure)
  - We understand the embrittlement problem and we have the means to tame it.
    - Similar experience with fatigue cracking in the aerospace industry