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

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2009 DOE Hydrogen Program Review

June 9, 2010

Project ID #
PD023

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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
  - FY2005: $180,000
  - FY2006: $80,000
  - FY2007: $473,010
  - FY2008: $166,090
  - FY2009: $0
  - FY2010: $300,900

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

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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.)
- 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
  - Simulated subcritical crack growth and crack initiation at MnS for natural gas pipelines
- 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

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Milestones for 2009-2010

- Go/no-go decision on the fracture mechanism
  - Rising-load fracture testing performed at Sandia National Laboratories. Fracture mechanism is currently under investigation. Strong evidence for ductile mechanism.
- Go/no-go decision on applicability of equilibrium models of hydrogen-induced change of interfacial cohesive energy
  - Decision was made to proceed with a non-equilibrium model
- 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 the use of *ab-initio* calculations. We continue work on calibrating the model parameters.
- Go/no-go decision on subcritical crack growth experiments
  - Decision was made not proceed with these experiments as they are difficult to perform and interpret for medium and low strength (i.e., pipeline) steels.
    - Hard to initiate cracking, conditions of K-dominance difficult to meet, role of plastic wake upon propagation unresolved
  - Instead, we are proceeding with rising load fracture testing to identify "Initiation thresholds" in the presence of hydrogen.
- Fracture mechanism combined with developed simulation tools will establish criteria for safe operation of pipeline steels under static hydrogen pressure conditions
  - Our experiments so far indicate that pipeline steel types B and D are fairly resistant to hydrogen: Fracture toughness greater than 40MPa $\sqrt{m}$ 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.

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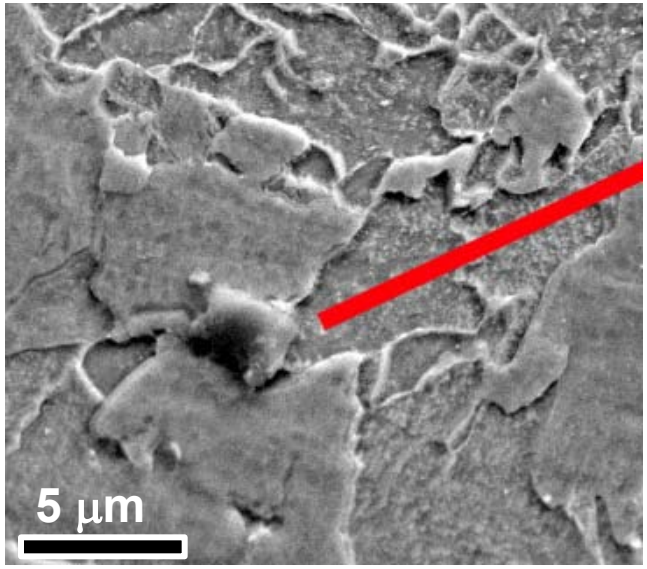
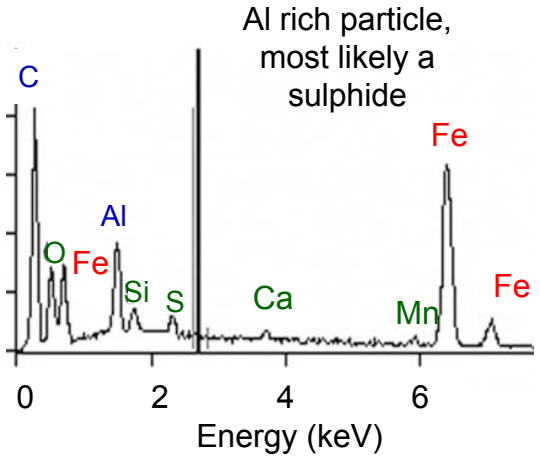
Technical Accomplishment: Microstructural Characterization

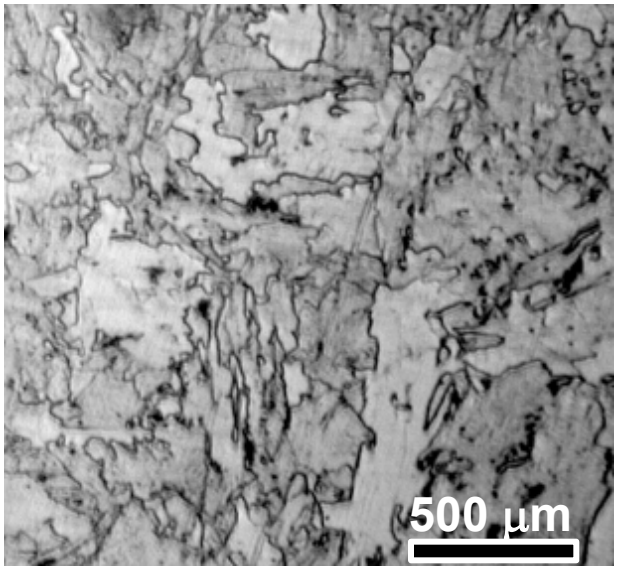
- Completed microstructural analysis of four "promising" pipeline steels provided by Oregon Steel Mills, and microstructures provided by Air-Liquide and Air Products
- Needed for hydrogen transport analysis

SEM analysis

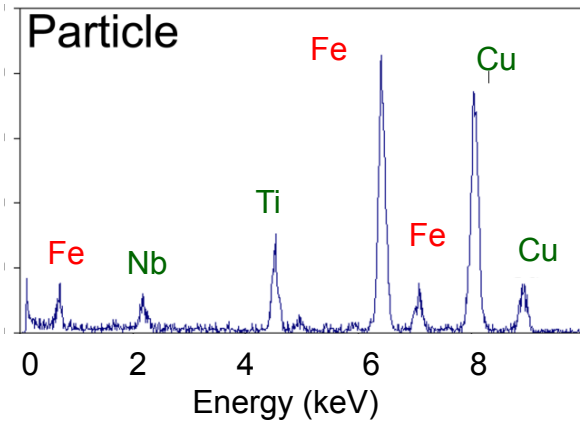


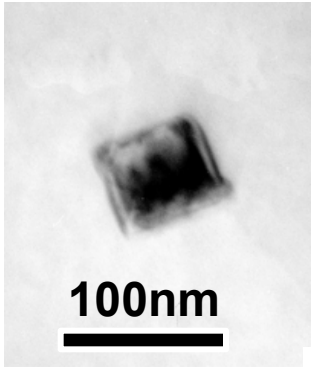


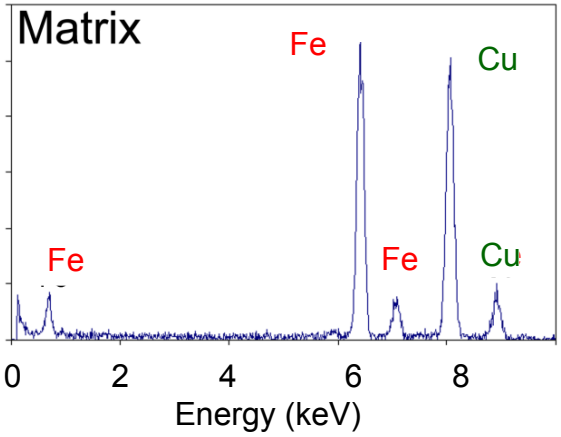
Optical microscopy



TEM image of a Ti, Nb particle







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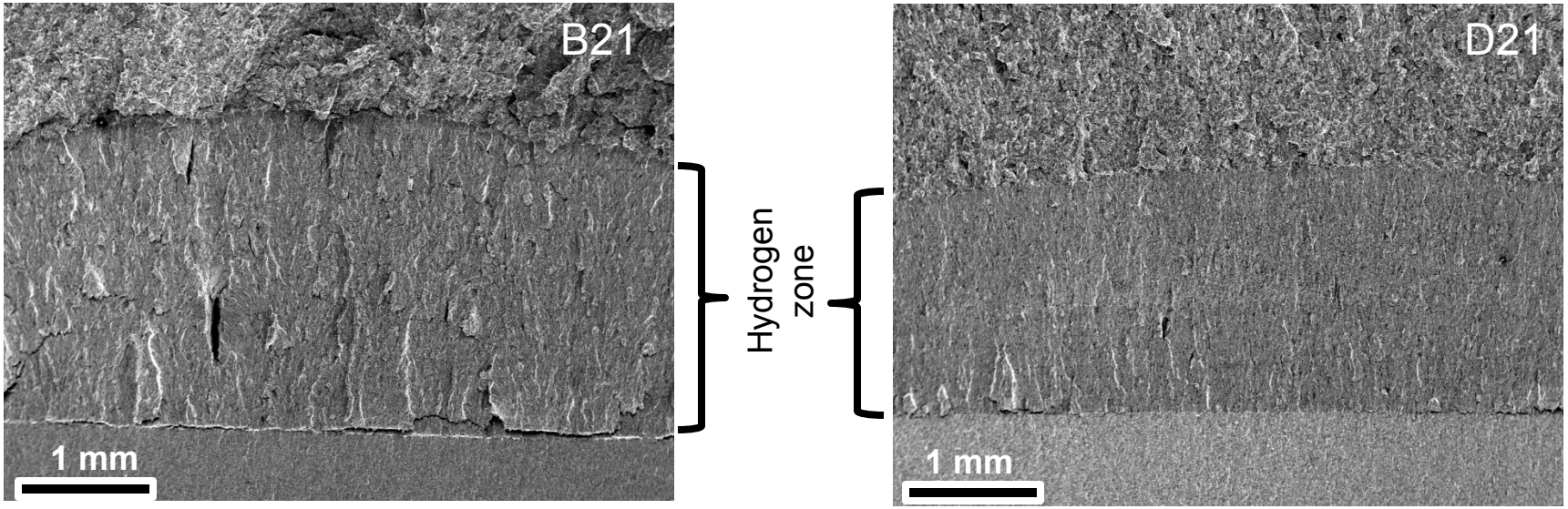
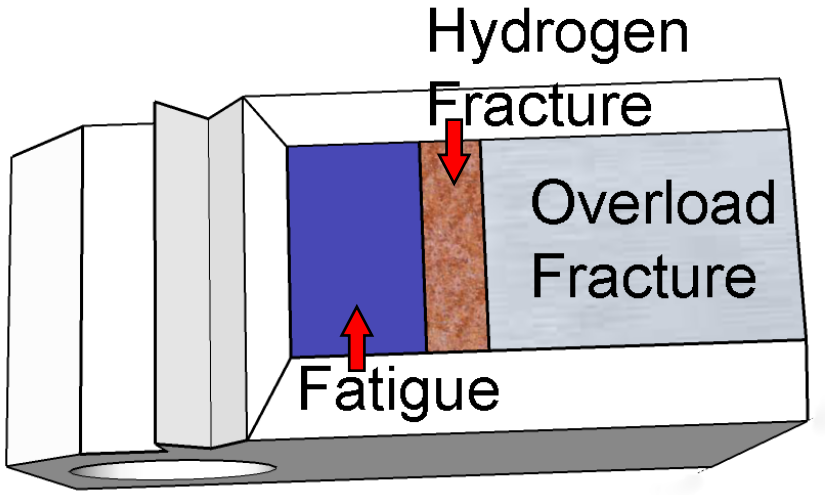
Technical Accomplishment: Wide-view SEM of Specimen B and D Fractured in 3 ksi H_2 gas



Images taken at Sandia

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



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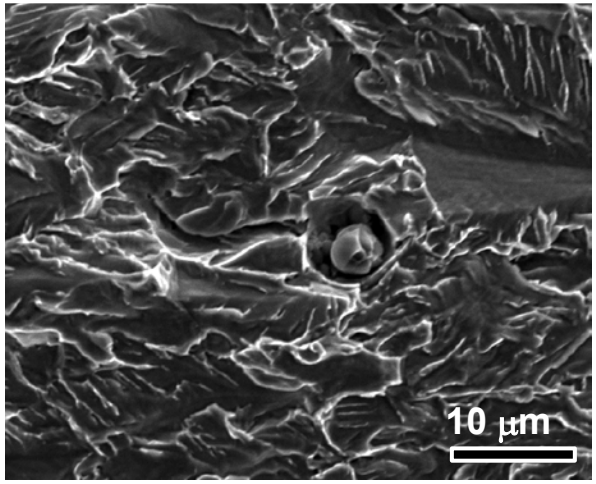
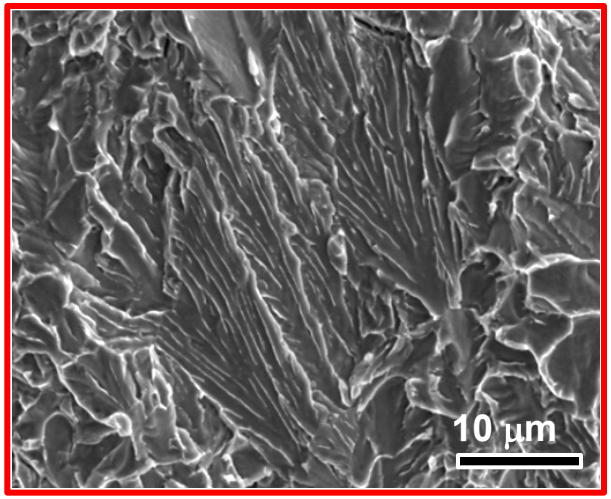
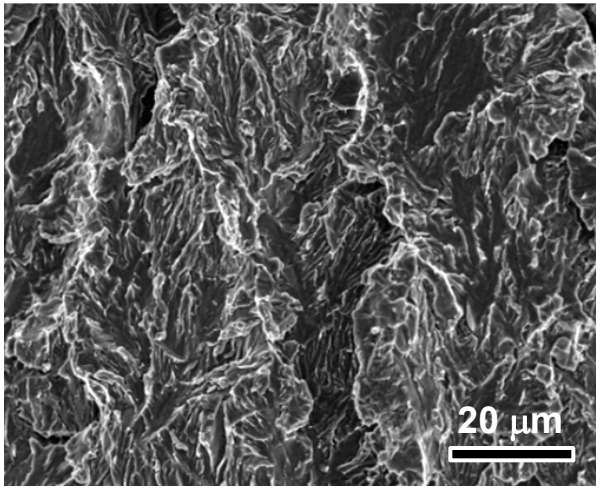
Technical Accomplishment: identification of different morphologies on the fracture surface

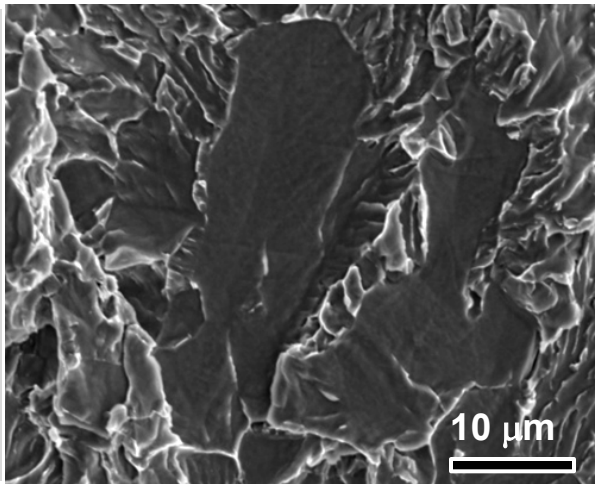


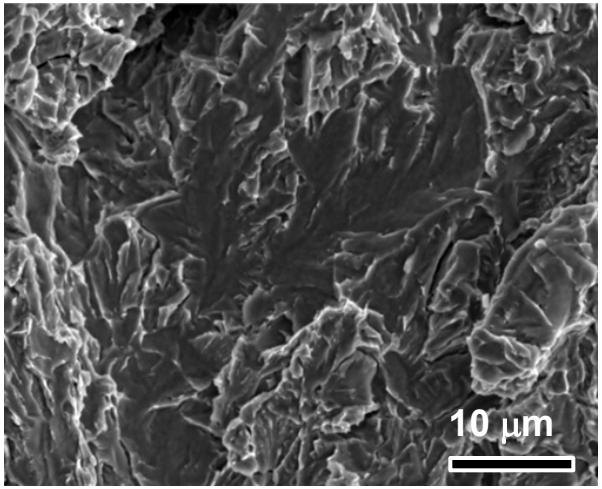




Need to understand how these morphologies relate to microstructure and hydrogen effects on it.

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





No compositional variation away from inclusions

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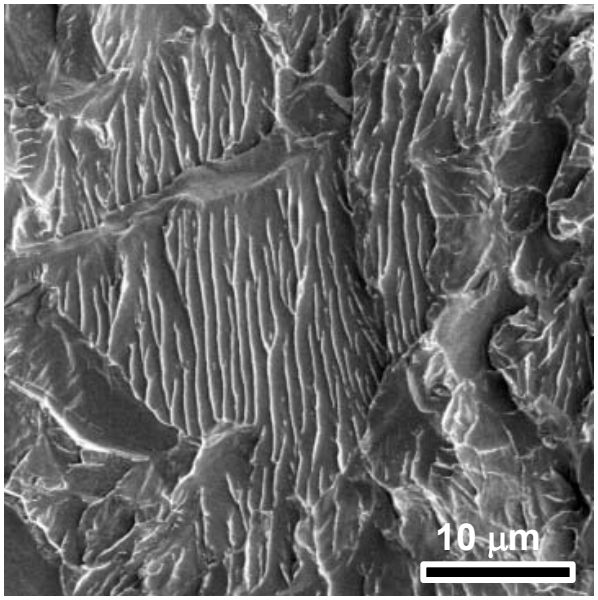
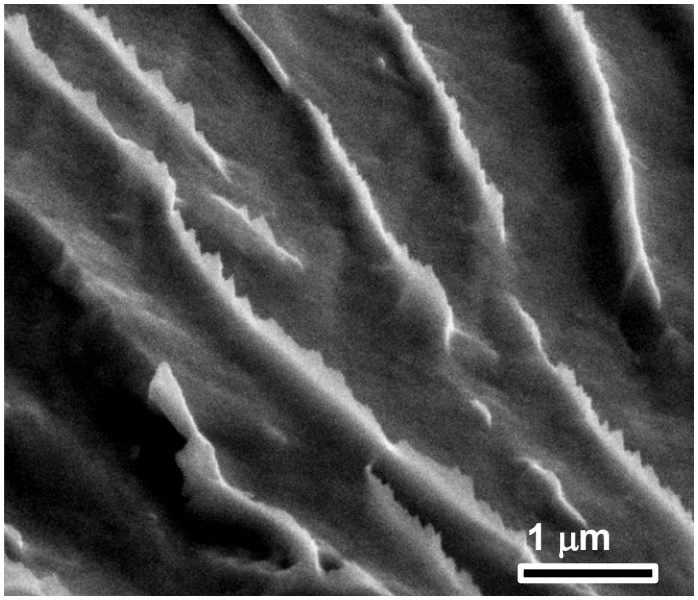
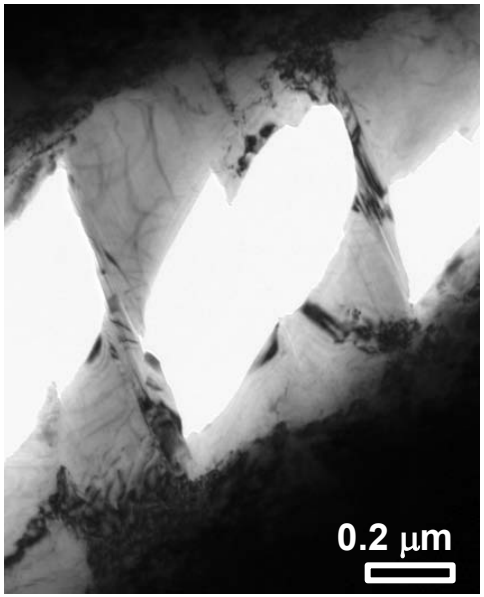
Technical accomplishment: unique features identified on fracture surface







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

The presence of the ridges suggest plastic processes but how are the related to hydrogen and the fracture mechanism?

TEM image of in-situ fractured Cu-3%Co sample showing saw-teeth due To final tearing. Image courtesy of G. Liu.

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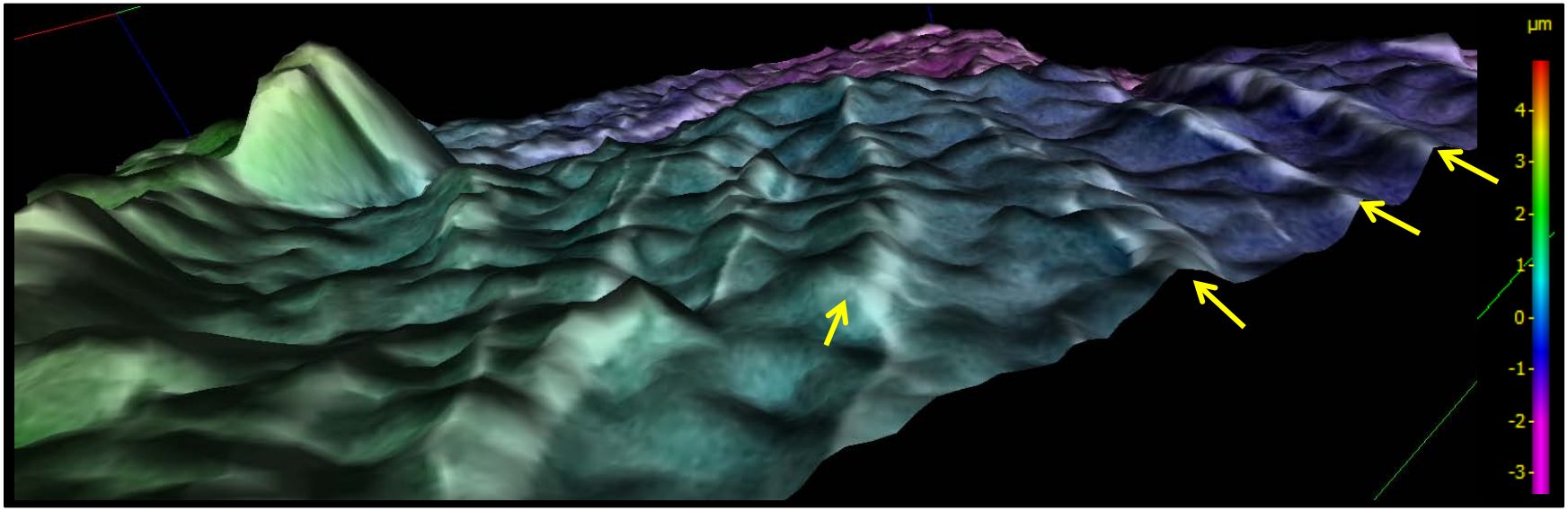
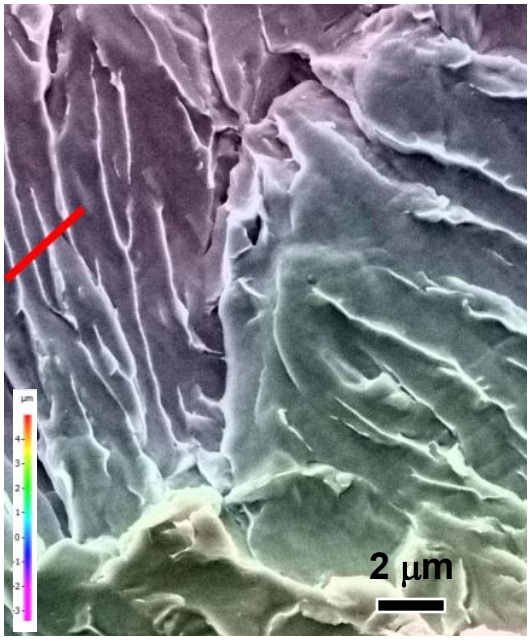
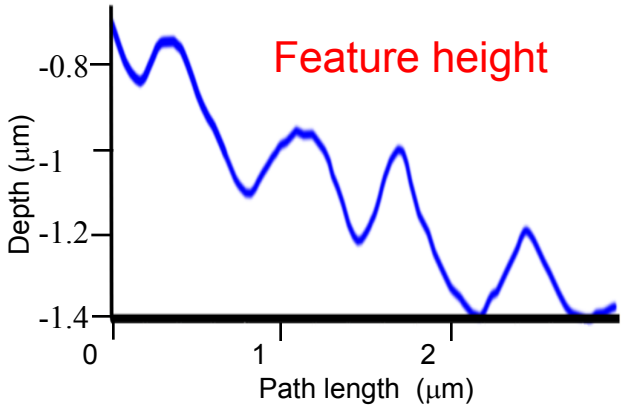
Technical Accomplishment: Surface topography revealed by 3D visualization







- 3-dimensional view reveals the surface topography confirming the ridge formation.
- Feature height measurement shows ridges are approximately protrusions of 400 nm.

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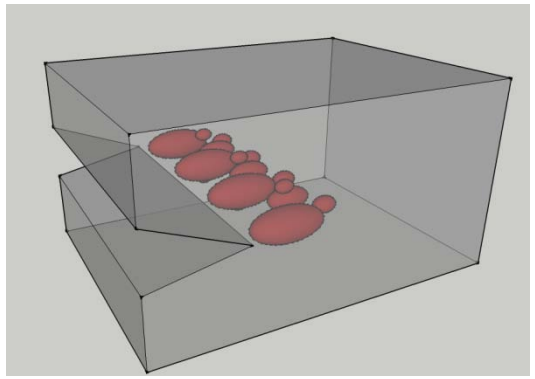
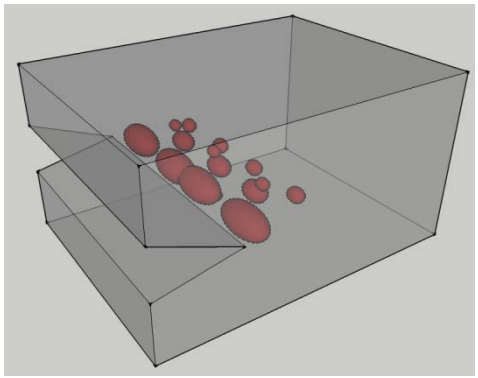
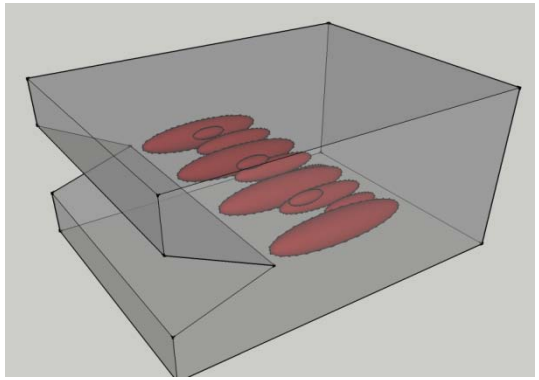
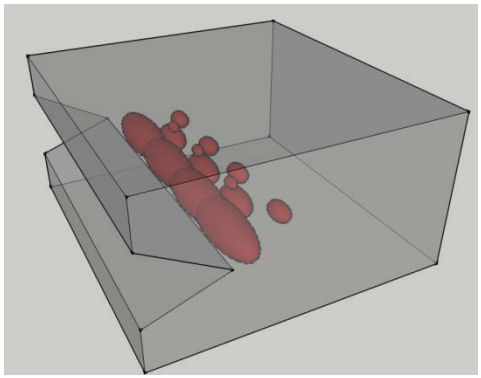
Possible microstructural features responsible for observed fracture surface

Void mechanisms





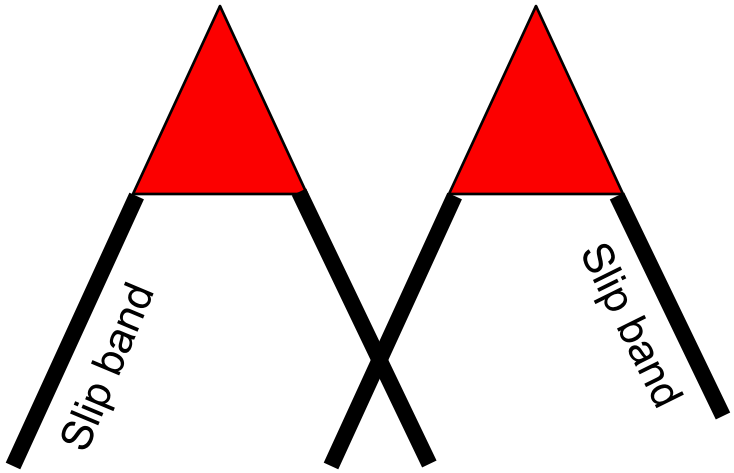




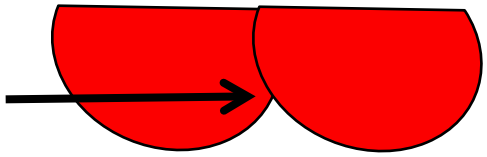
Growth normal to crack front

Growth parallel to crack front

Slip band mechanism



Differentiate by determining the microstructure directly beneath the fracture surface



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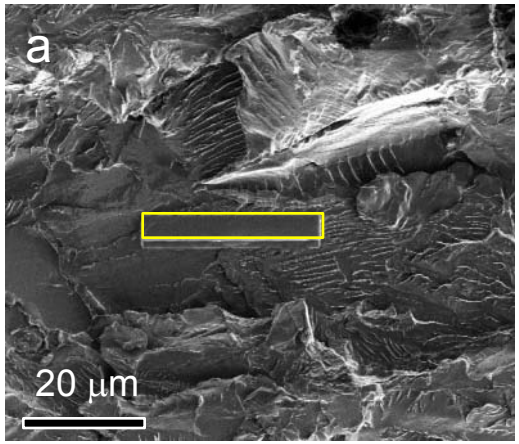
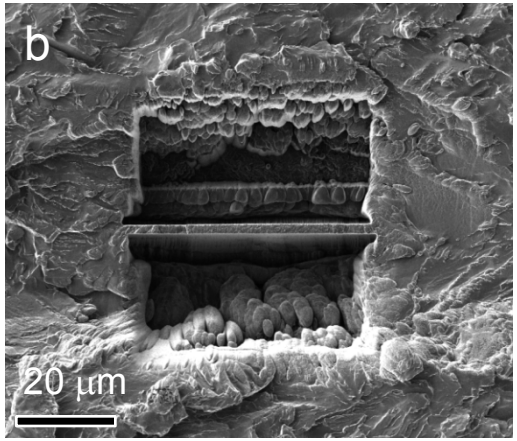
Technical Accomplishment: Site specific sample extraction from a rough surface using Focused Ion Beam Machining

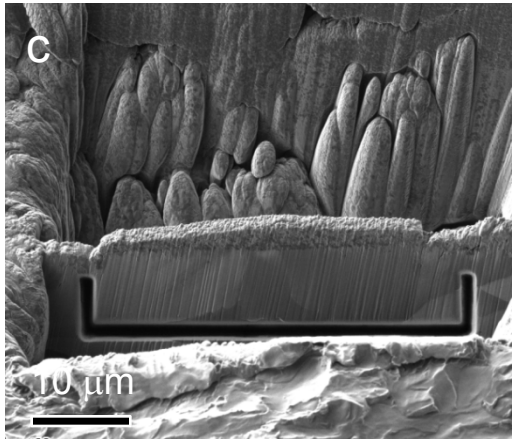
Select site, deposit Pt strip to identify and protect region

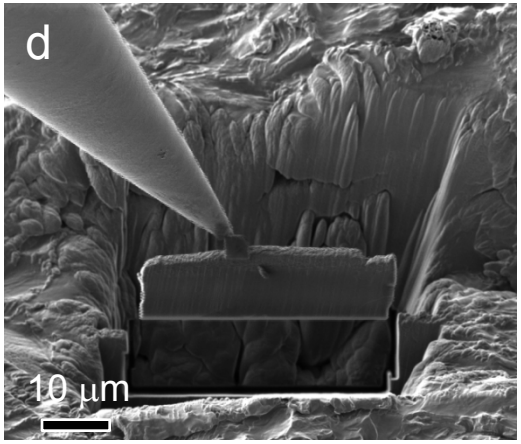
Machine out trenches on either side

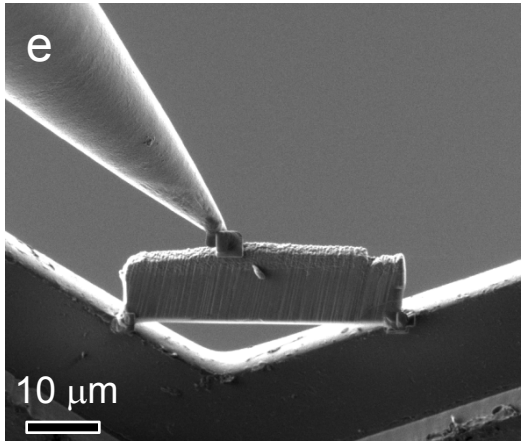
Make U-cut

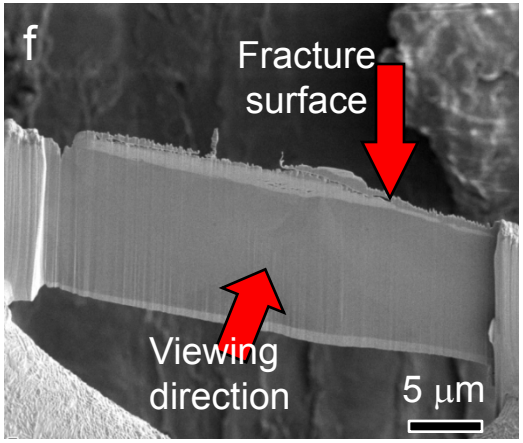












Attach needle to top of sample with Pt. Cut sample free by milling away remaining bridges and lift out

Attach sample to copper grid with Pt. Cut needle free from sample.

Attach sample to copper grid with Pt. Cut needle free from sample.

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Technical Accomplishment: Discovery of the mechanism responsible for “quasi-cleavage” fracture.

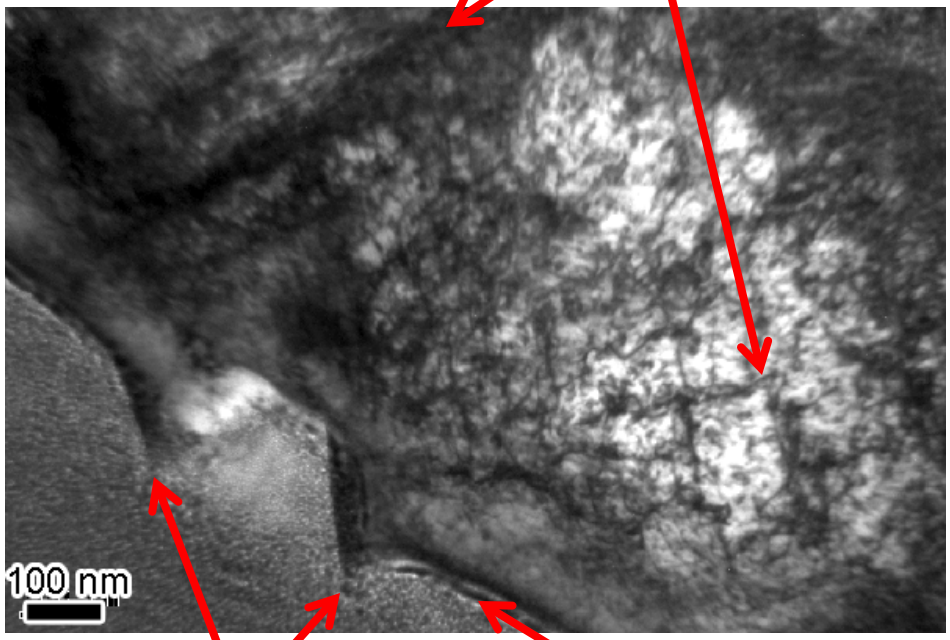

Image shows slip bands parallel to ridge edges, suggesting “quasi-cleavage is not a cleavage like process but is related to dislocation slip. Enhanced and confined slip activity is consistent with hydrogen enhanced local plasticity mechanism.

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

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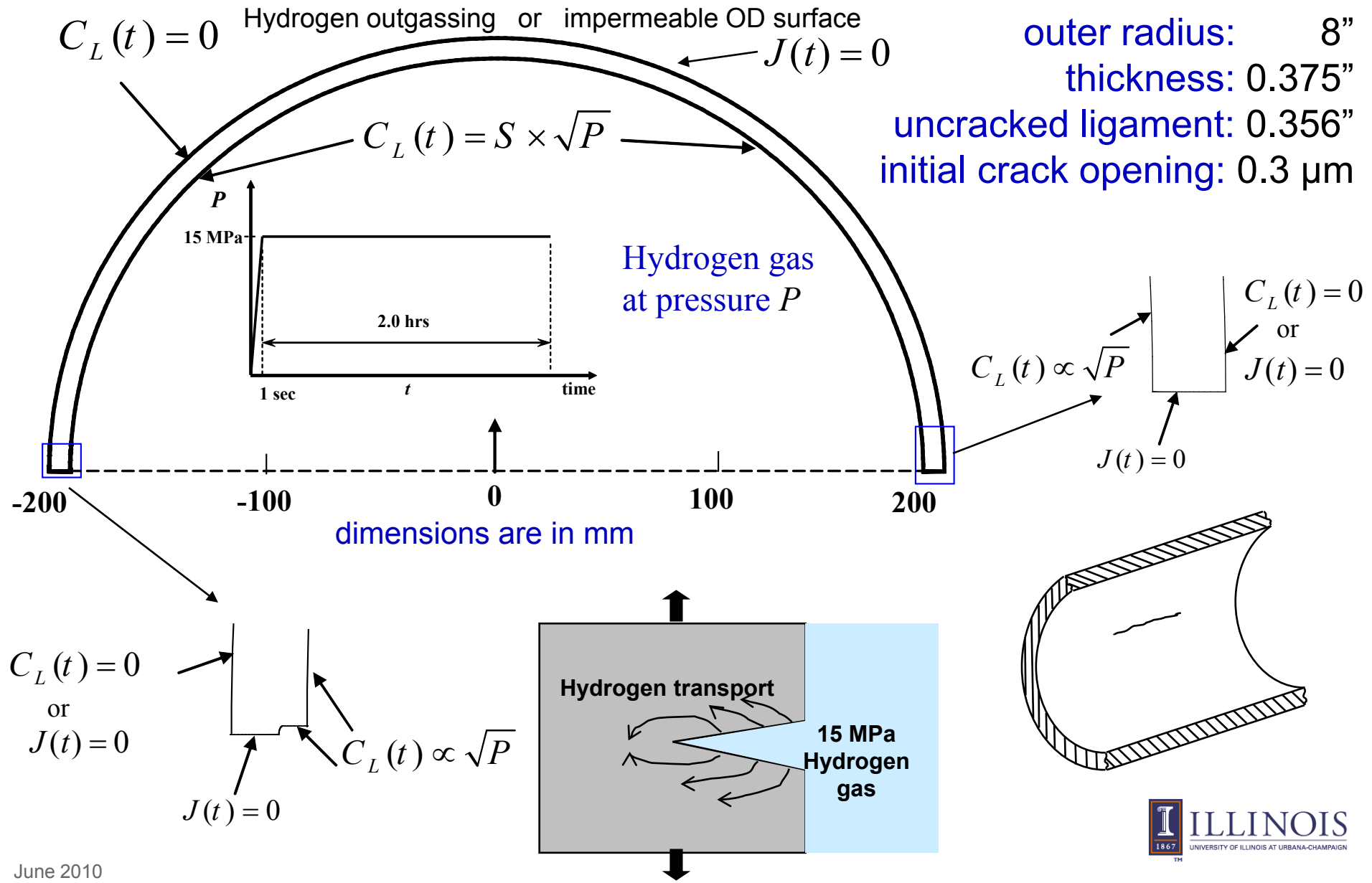
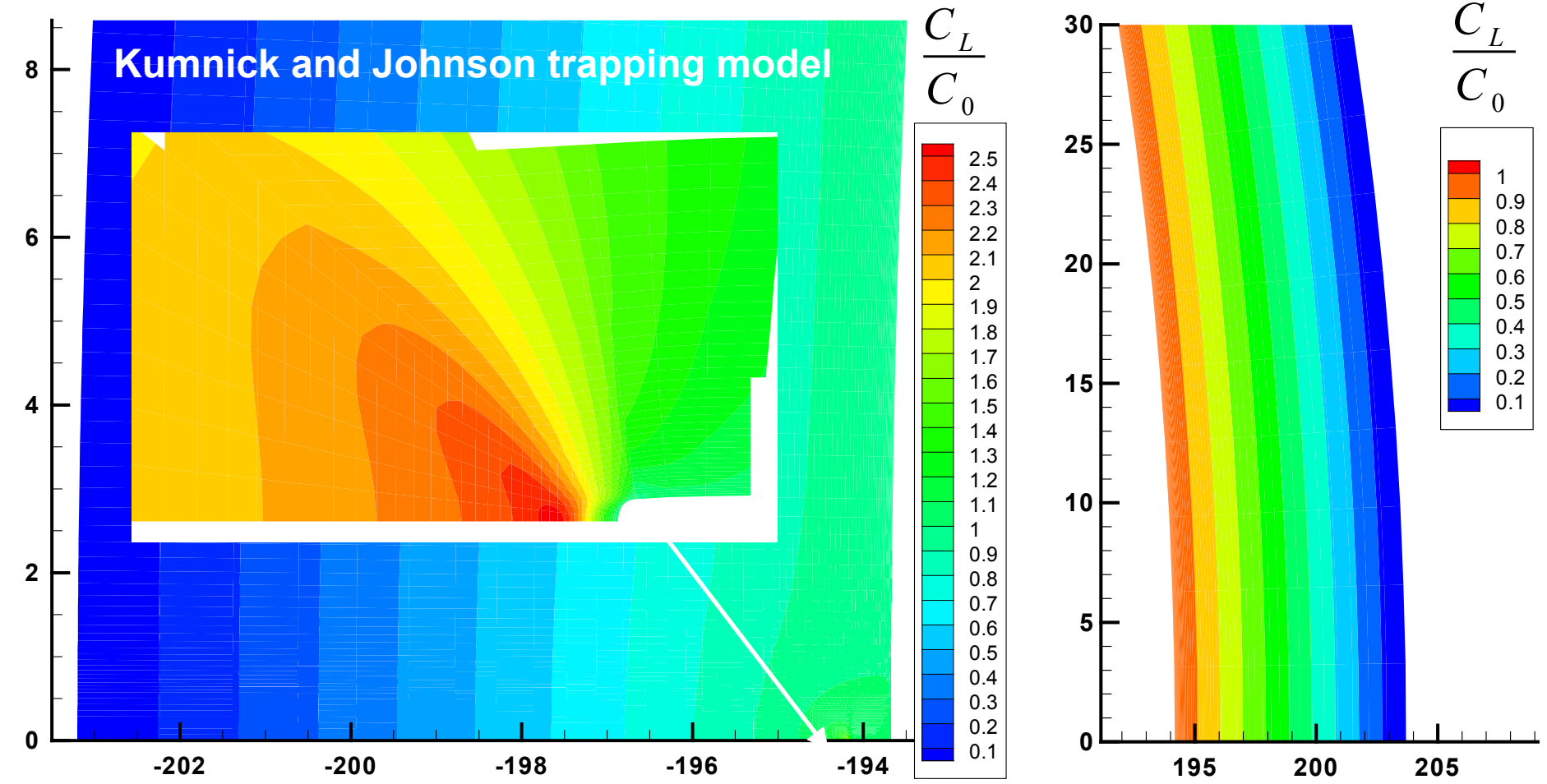
Technical Accomplishment: Analysis of Cracked Pipeline



Technical Accomplishment
Hydrogen Concentration at Steady-State

Time to steady-state: 2.0 hr



$C_0 = 2.65932 \times 10^{22}$ H atom / m^3 **corresponds to lattice concentration at** $P = 15$ MPa

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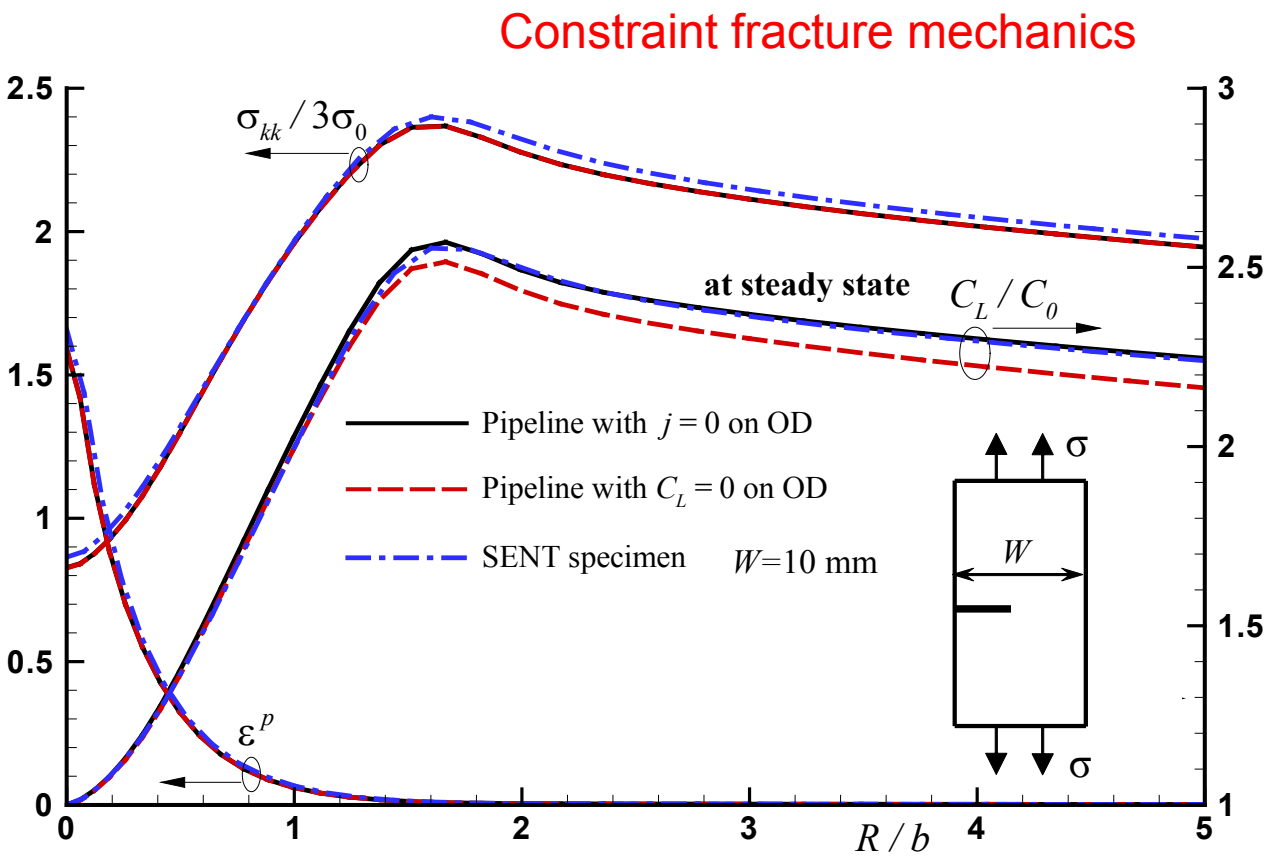
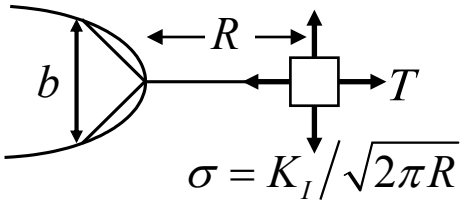
Technical Accomplishment: Environmental Similitude with Single Edge Notch Tension





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

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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

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Collaborations

- **ASME Codes and Standards**
  - Collaboration on safety factor calculations for hydrogen pipelines

- **International Collaborations (Japan)**
  - **Institute for Hydrogen Industrial Use and Storage (HYDROGENIUS) at Kyushu University, Fukuoka, Japan**
    - Collaborative research agreement between Kyushu and Illinois was signed on February 4, 2008 for faculty and student exchanges
    - Annual visits to the Institute by the project PIs.
    - Collaboration on all aspects of embrittllement (e.g., fundamentals, microstructural analysis, experiments, simulations)
  - **Annual meetings with HYDROGENIUS and the Automobile Industry of Japan (Toyota, Honda, Nissan) on Hydrogen Technology Standards**

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Future Work

Remaining of FY10

- **Experiment**
  - Characterization of fracture surfaces to establish the fracture mechanisms under static load conditions
  - Carry out additional rising-load fracture toughness testing (if needed) to clearly assess the hydrogen effect on fracture initiation
  - Start experiments under cyclic loading to assess fatigue resistance

- **Modeling and Simulation**
  - Integrate modeling and simulation with experiment
    - insertion of the fracture mechanism in our hydrogen/deformation finite element codes
    - Associate the fracture mechanism at the microscale with valid macroscopic indices of embrittlement
  - Use modeling to guide experiments with regard to the parameter space
    - Similitude (mechanical and environmental)
    - Pressure course (frequency, wave, etc.)

- **Devise fracture criteria for pipeline design under static hydrogen pressure**
  - Initiation threshold K_{th} as a function of hydrogen pressure

FY11

- **Focus on 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

$$da/dN \; vs. \; \Delta K$$

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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
- Unique identification of hydrogen-induced fracture mechanisms through FIB/TEM
- Thermodynamic theory for hydrogen-induced decohesion developed
- 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

Collaborations

- Active partnership with Sandia National Laboratories, Los Alamos National Laboratory, ASME codes and Standards, JAPAN (Hydrogenius Institute), Industrial Partners (e.g. ExxonMobil, SECAT)

Proposed future research

- Fracture testing (rising-load toughness) and simulation of the fracture process
- Quantify initiation threshold in the presence of hydrogen
- 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

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Supplemental Slides

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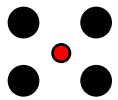
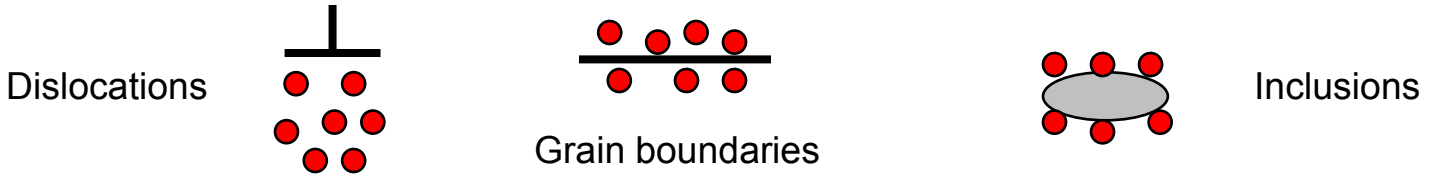
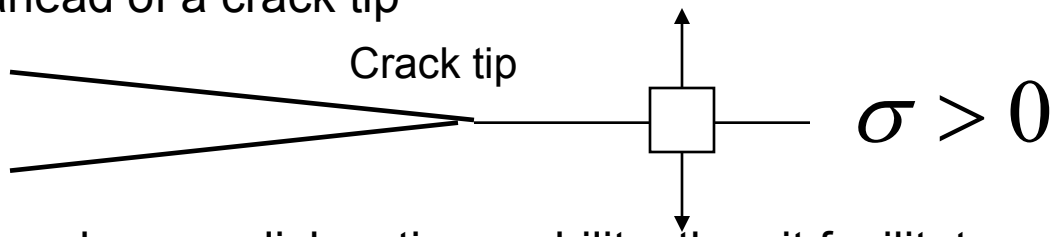
Technical Accomplishment: Hydrogen Transport Model

- Diffusing hydrogen resides at
  - **Normal Interstitial Lattice Sites (NILS)**  C_L
  - **Trapping Sites** C_T
    - Microstructural heterogeneities such as dislocations, grain boundaries, inclusions, voids, interfaces, impurity atom clusters



- Diffusing hydrogen interacts with stresses and strains
  - **Hydrogen dilates the lattice and thus interacts with hydrostatic stress**
    - Moves from regions under compression toward regions under tension, e.g ahead of a crack tip



  - Hydrogen enhances dislocation mobility, thus it facilitates plastic flow

- As hydrogen diffuses stresses and strains change. At the same time local stresses and strains affect the diffusion paths. The problem is coupled, and solution involves iterations

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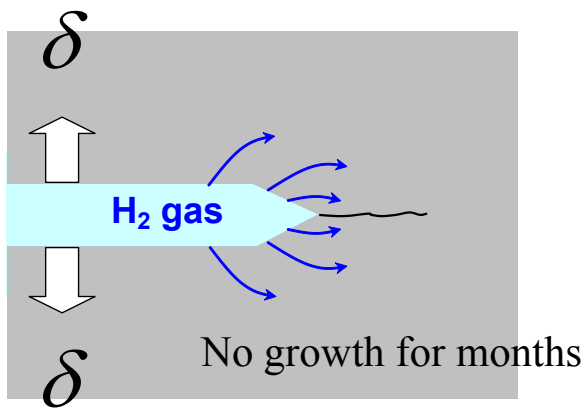
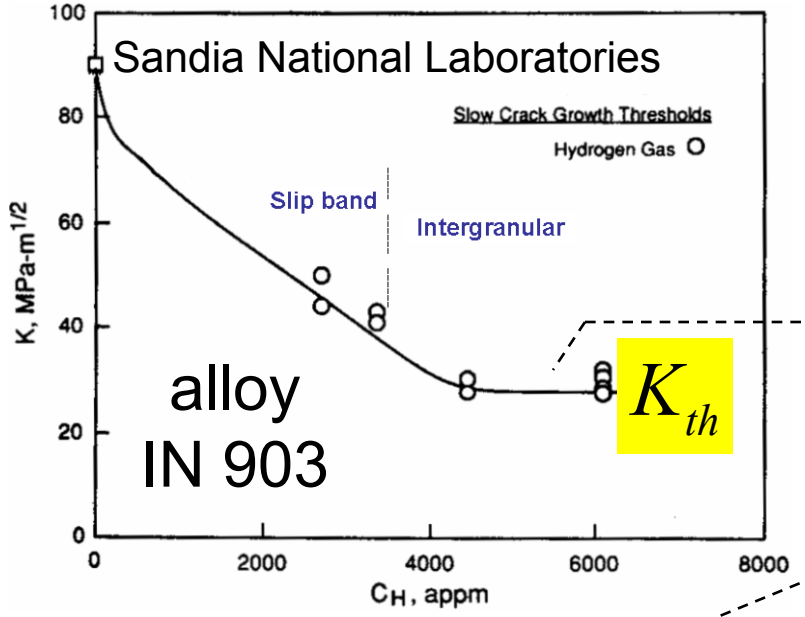
Simulation of Sustained-load Intergranular Cracking

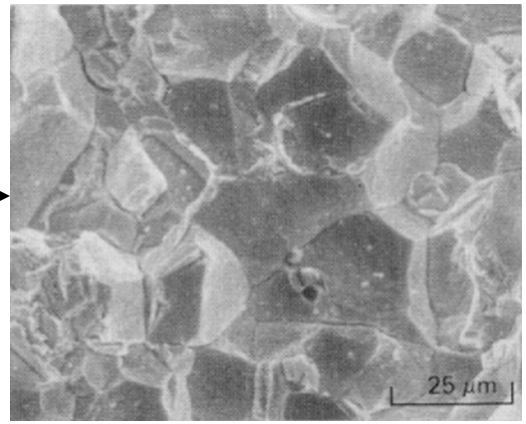
Technical Accomplishment

Wedge Open Load (WOL) specimen

First bolt-load the specimen and then expose to hydrogen gas at different pressures







- Simulate controlled intergranular cracking through cohesive element methodology
- Grain boundary cohesive stress is furnished by thermodynamic theory of grain-boundary decohesion
- Objective is to predict K_{th}

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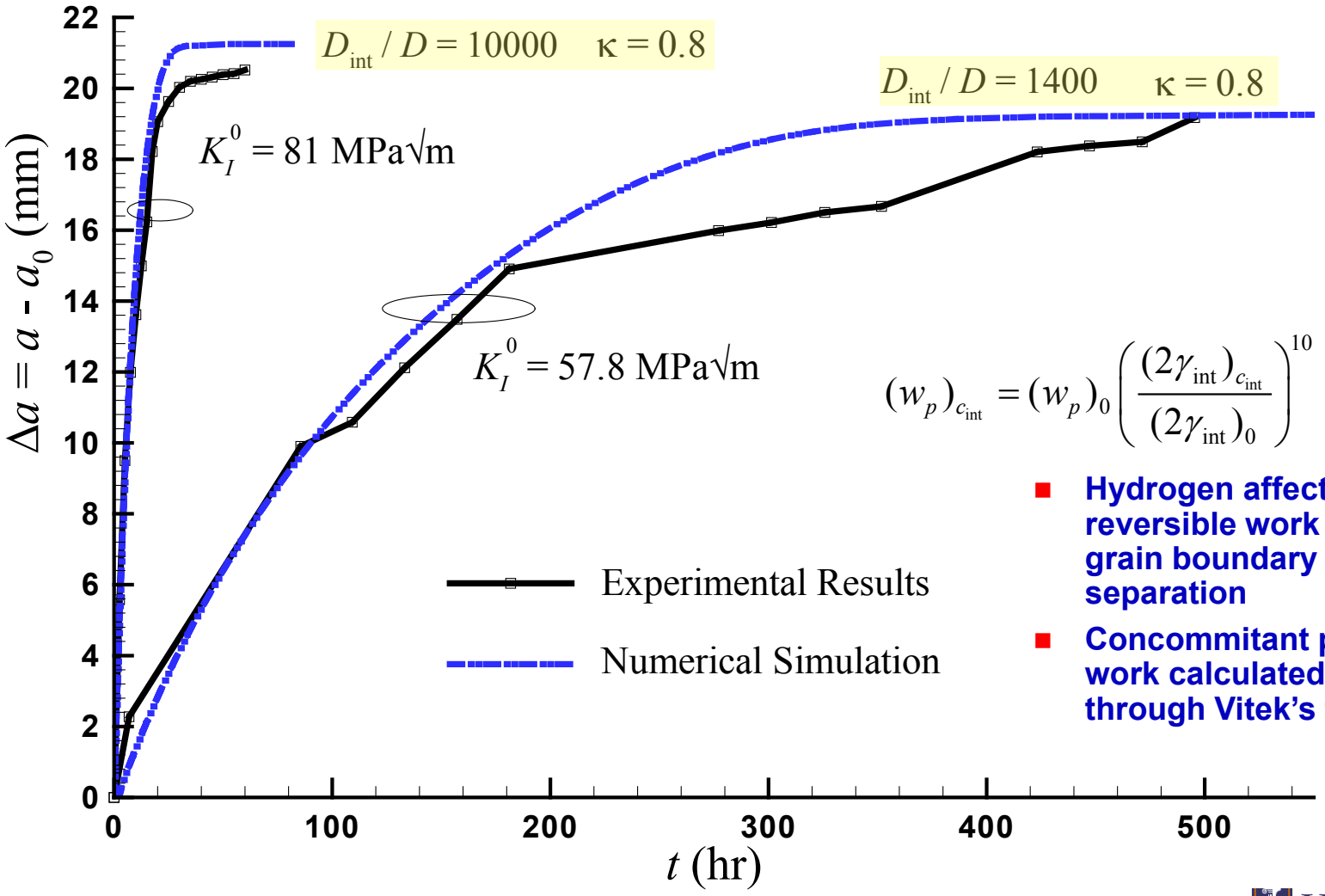
Technical Accomplishment: Simulation of Intergranular Cracking Kinetics



- **Hydrogen affects reversible work for grain boundary separation**
- **Concommitant plastic work calculated through Vitek's theory**

Effect of initial loading K_I^0

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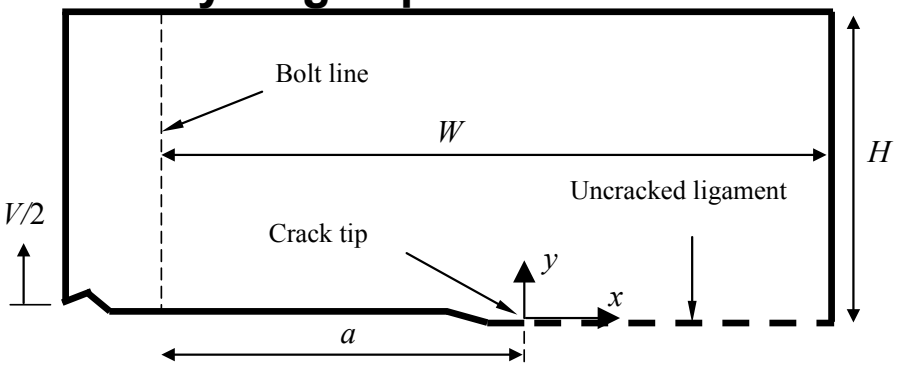
Simulation of Sustained-load Intergranular Cracking

Technical Accomplishment

Hydrogen pressure 207 MPa



Initial crack length: $a_0 / W = 0.471$

Initial month opening: $V_0 = 0.5588\,\text{mm}$

$$K_{IC} = 90\,\text{MPa}\sqrt{\text{m}}$$

Load at $K_I^0 = 57.8\,\text{MPa}\sqrt{\text{m}}$

Threshold $K_{th} = 33.5\,\text{MPa}\sqrt{\text{m}}$

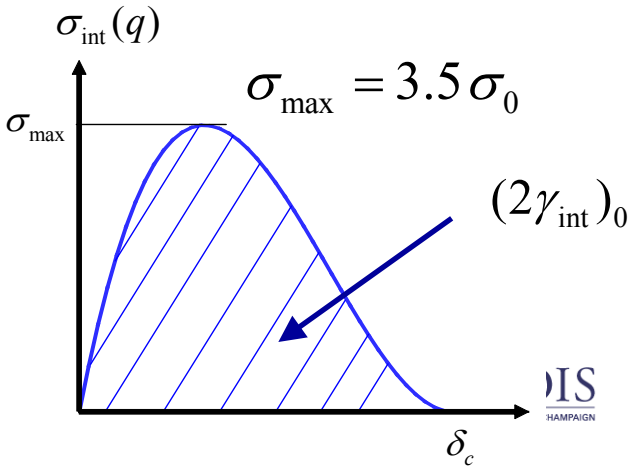
Grain-Boundary Traction-Separation Law

$$\sigma(\theta_{\text{int}}, q) = \frac{27}{4}\sigma_{\max}\left[1 + (\kappa - 1)\theta_{\text{int}}\right] q(1-q)^2$$

H-concentration at grain boundary

Grain-boundary separation= $q = u_n / \delta_n$

$\sigma_{\max}$ = maximum cohesive stress in the absence of hydrogen

$$\kappa = \frac{(2\gamma_{\text{int}})_{\theta_{\text{int}}=1}}{(2\gamma_{\text{int}})_0} = \frac{\text{cohesive energy of saturated GB}}{\text{cohesive energy of hydrogen-free GB}}$$

$$(2\gamma_{\text{int}})_0 = \frac{K_{Ic}^2(1-\nu^2)}{E} \approx 52\ \text{kJ/m}^2 \qquad \kappa = \left(\frac{33.5}{90}\right)^2 = 0.138$$