International Institute for Carbon-Neutral Energy Research

Outline and Future Perspectives

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A World Premier Institute

There is no Time more Opportune for such an Effort (President Obama visited Tokyo on Nov. 13, 2009)

Announcement of initial areas relevant to the Proposed Institute of Kyushu University for joint activities to strengthen US/Japan cooperation

- **Acceleration of joint activities between national laboratories of the United States and Japan through R&D cooperation, exchanges of information, knowledge and researchers, workshops and conferences, and collaboration on standards research**
- **Cooperation on carbon capture and storage including modeling, testing and data sharing for the purpose of prediction and mitigation of the possible risks, and the development of new capture methods, simulation tools and monitoring methods**
- **Enhancement of cooperative research, development and deployment activities in additional areas including basic research, renewable, energy efficient buildings, and next generation vehicles**
- **Close cooperation on energy issues and the development of joint projects in multilateral frameworks including the Major Economies Forum on Energy and Climate (MEF), International Energy Agency (IEA), the Asia-Pacific Partnership on Clean Development and Climate (APP), the International Partnership for Energy Efficiency Cooperation (IPEEC), the International Renewable Energy Agency (IRENA) and especially, the Asia Pacific Economic Cooperation (APEC) which Japan chairs in 2010 and the United States in 2011.**

http://www.whitehouse.gov/the-press-office/fact-sheet-us-japan-cooperation-clean-energy-technologies

I²CNER

World Premier Research Center Initiative

- **Japan Ministry of Education, Culture, Sports, Science and Technology (MEXT)**
- **Japan Society for the Promotion of Science (JSPS)**

- **Objectives**
  - Advance cutting-edge interdisciplinary research
  - Establish an international research environment within Japan with global visibility
    - Invite the best from around the world within a host institution
    - 30% foreign researchers
  - Help reform the Japanese university system—impact the university culture
    - New criteria for faculty hiring, promotion, and compensation
    - Research organization culture
      - Assistant professors
    - Independent management of institute
    - English is the official institute language

- **Magnitude**
  - 20 Principal Investigators (faculty)
  - A total of 200 researchers (faculty, post-docs, graduate students)

- **Funding**
  - 1.35 billion yen ($16 million) per Institute per year
  - Support over 10-15 years

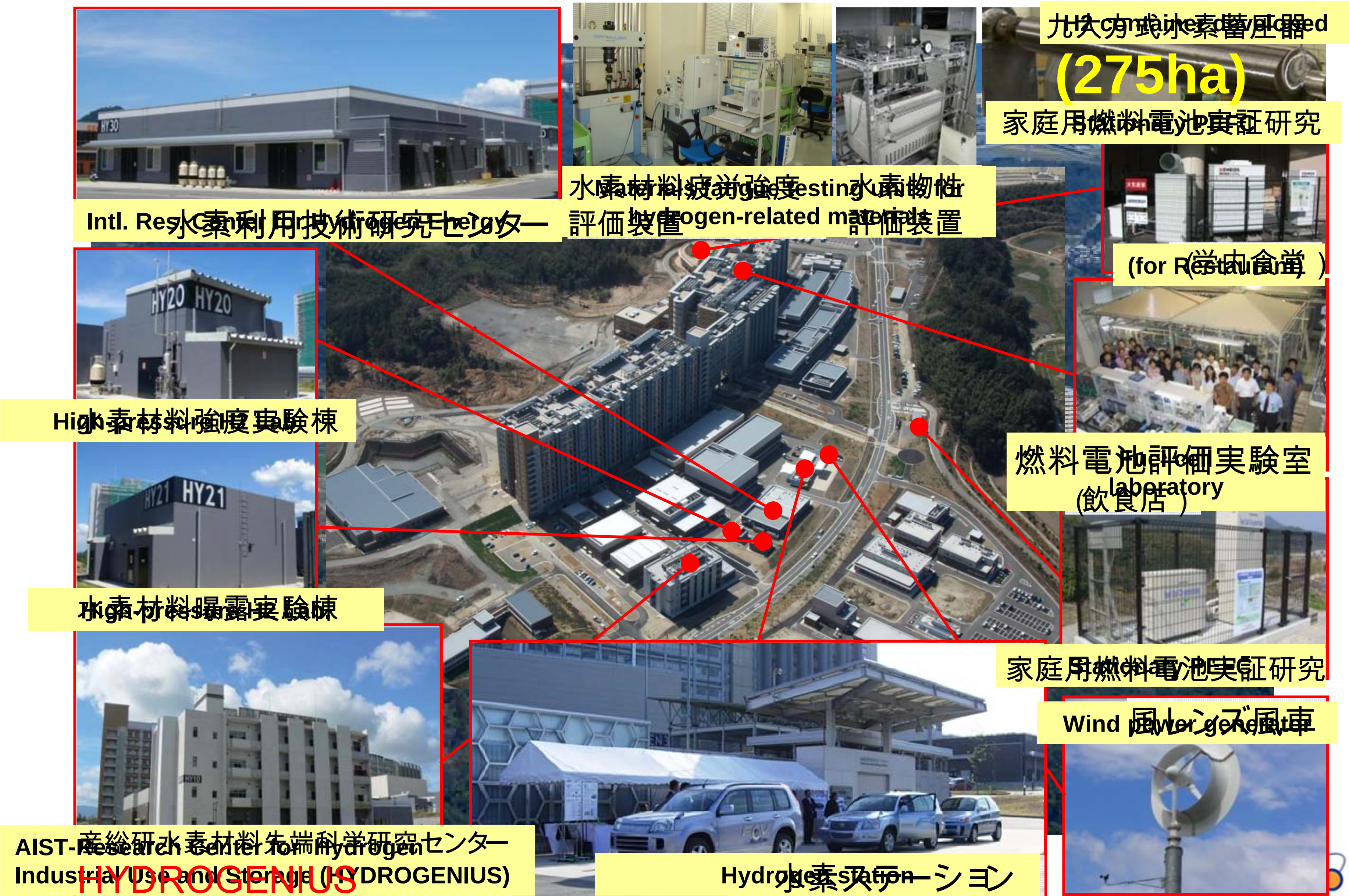
International Institute for Carbon-Neutral Energy Research

- Long and ongoing collaborative research relationship on hydrogen in materials
  - Kyushu University (Murakami)
  - University of Illinois (Sofronis, Robertson)
    - Research at Illinois funded by the Fuel Cell Technologies Program of DOE
  - Sandia National Laboratories, Livermore (Somerday)
  - University of California, Berkeley (Ritchie)

  } HYDROGENIUS Institute for Hydrogen Industrial Use and Storage
- MEXT issued call for white papers in February 2010
- Kyushu/Illinois submitted proposal in April 2010
- Proposal document review in June 2010
- Reverse site visit at MEXT on July 13, 2010
  - 4 competing proposals
  - High-power review committee
    - Former US NSF Director, Physics Nobel Laureate (2008), Chemistry Nobel Laureate (2001)
- Winner
  - International Institute for Carbon-Neutral Energy Research (Kyushu University)
    - Advanced Institute for Materials Research (Tohuku University)
    - Institute for the Physics and Mathematics of the Universe (University of Tokyo)
    - Institute for Integrated Cell-Material Science (Kyoto University)
    - Immunology Frontier Research Center (Osaka University)
    - National Institute for Materials Nanoarchitectronics

- Institute was launched on December 6, 2010
- Kick-off Symposium on February 1, 2011
  - Participation from Kyushu, Illinois and other partners (MIT, ETH, Imperial College)

Kyushu University:World Class Facilities



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I[2]CNER Goals

- **Advance fundamental science on Carbon-Neutral Energy Research to remove the barriers for a hydrogen-powered society and CO_2 capture and storage (CCS)**
  - Multi/Interdisciplinary approach to the study of interactions between hydrogen/CO_2 and materials
    - Solid/Fluid mechanics, Chemistry, Physics, Materials, Geoscience, Oceanography
  - Elucidate underlying fundamental mechanisms
    - e.g., adsorption, absorption, dissolution, diffusion, reaction

- **Enable innovative technologies**
  - Hydrogen production, hydrogen storage materials, hydrogen embrittlement resistant materials, next generation fuel cells, material transformation catalysts; CO_2 separation and concentration; CO_2 geo- and sub-seabed sequestration

- **Enhance public awareness on hydrogen-powered society and CCS**
  - Society decisions based on sound scientific information
    - e.g., long term effects of CO_2 on marine environment

I^2CNER Programmatic Structure

- **Educational**
  - Exchange Graduate students, post-docs, and faculty
    - Adjunct appointments at Kyushu and Illinois
- **Institutional**
  - Kyushu
    - Foster an international environment by establishing an international network to promote fundamental research
    - New criteria and expectations for faculty hiring, development, promotion, and compensation
    - Independent management of Institute and decision making
  - Illinois
    - Advance research collaborations with Japan
- **Academic/Scientific community**
  - High visibility conferences and workshops on key challenging topics
    - Output: identify key roadblocks – these will guide the research agenda
    - Annually, alternating between Kyushu and Illinois
  - *2012 International Conference on Hydrogen Effects on Materials*
  - *CCS Summer School by the International Energy Agency Green House Gas (IEAGHG)*

Leverage and Impact

- **USA (NSF—Key opportunities)**
  - **NSF International Programs (Target Japan)**
  - **NSF ties with DOE (EERE/BES), in particular in the hydrogen area**
  - **International Materials Institute awards**
  - **Kyushu, Illinois, Berkeley, Sandia, Imperial College, ETH, Gottingen, Max-Planck-Institute in Dusseldorf, University of Thessaly (Greece)**

- **JAPAN**
  - **Fukuoka Strategy Conference on Hydrogen Energy**
    - **Mr. Aso, Governor of Fukuoka Prefecture**
    - **Strong presence of Toyota Motor Corporation**
  - **HYDROGENIUS**
    - **New Energy and Industrial Technology Development Organization (NEDO)**

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Establishing I^2CNER as Center on Energy and Sustainability Research

- **Foster new research initiatives through annual research competition**
  - Process
    - White paper and presentation
    - Based on the LDRD program at the US National Laboratories
    - Involve the External Advisory Committee
  - Frequency
    - annually
  - Two-year funding
  - Use network with partners, national laboratories, funding agencies to promote KYUSHU/ILLINOIS led research initiatives

I^2CNER Technical Activities

H_2
➔ Production, Storage, and Distribution

CO_2 in Earth and Ocean
➔ Risk Management of CCS

Solar H Production
Artificial Photosynthesis

Thermophysical properties (H_2, CO_2)

Optimum and Intelligent Material Transformations (waste-free)

Efficient Hydrogen Storage Materials

Hydrogen Structural Materials (compatible with hydrogen)

Next Generation Fuel Cells (novel materials and devices)

CO_2 Separation Concentration (low energy separation)

CO_2 Geological Storage (Chemomechanical interactions of CO_2 with rock and fluids)

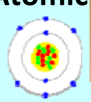
CO_2 sub-seabed Sequestration (CO_2/Ocean-turbulence interaction)

Understanding Interface-gas reactions

H_2 CO_2

absorption, adsorption, dissolution, diffusion, reaction, conduction, etc.

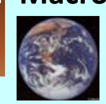
Atomic



Spatial scale — Matter

molecular -- earth, ocean

Macro



Nanoseconds - - - decades

Temporal scale

Bio-mimetics | Chemistry | Physics | Materials Science | Mechanics | Oceanic Science | Geo-Science

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Hydrogen Embrittlement

- **Roadblocks**

  Lack of understanding of how the degradation mechanisms bring about material failure

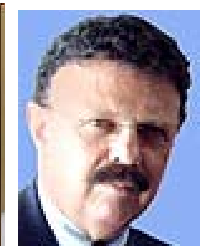
- **Goals**
  - Understand fundamental interactions of hydrogen at the atomic scale and microscale in metals and alloys
  - Understand the kinetics of hydrogen/microstructure interactions
  - Design materials with known resistance to hydrogen embrittlement

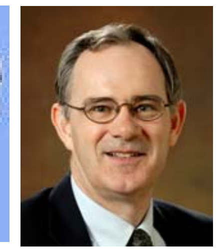

S.Matsuoka


Y.Kondo


J.Sugimura

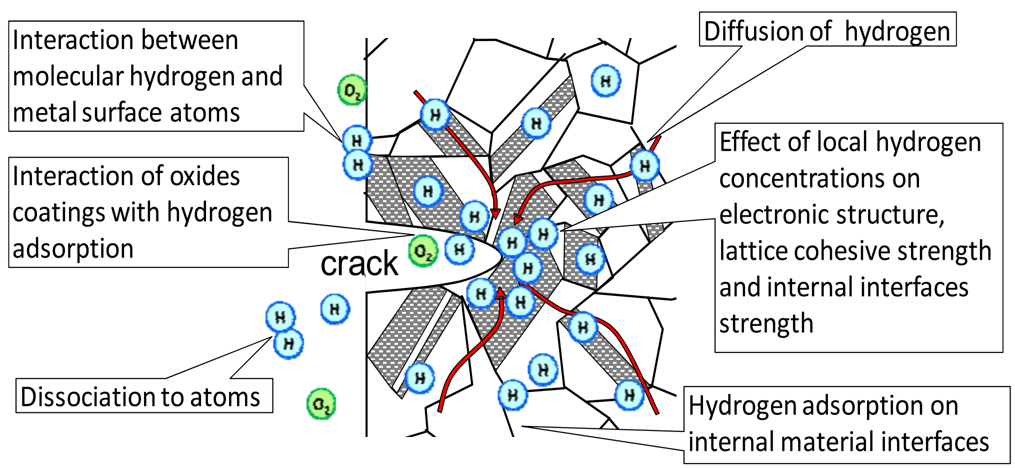

B. Somerday


R.Ritchie


I. Robertson

- **Technical approach**

  Synergistic experimental and computational methodologies to discover
  - H adsorption rates
  - Effect of local H on the local electronic structure, lattice cohesion, and strength of internal interfaces
  - H interaction with dislocation cores
  - H treatment in material constitutive models
  - Fundamental mechanisms of fatigue



Pressing Issue: Hydrogen-Induced Fracture Prognosis

- **Criteria for monitoring the onset of fracture instability are needed**
  - Codes and standards for reliable and safe operation of material components that are mechanism-based
  - Current design guidelines for pipelines apply, in some cases, arbitrary and conservative safety factors on the applied stress

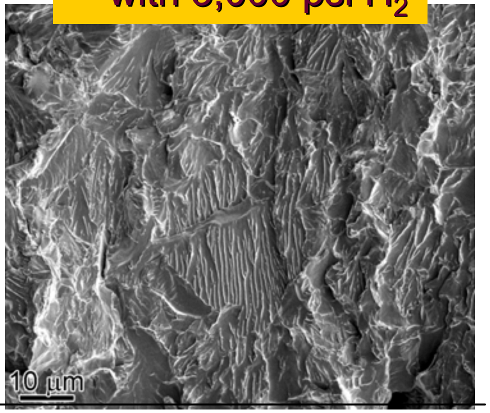
- **Quasi-Cleavage fracture**

Medium-strength steel

Typical pipeline low carbon (0.03% by wt) Mn-Si-single microalloy API/Grade X60 steel

•Features of fracture surface, Surface topography
•Sample extraction by Focused Ion Beam (FIB) machining
•TEM analysis
•Nature of the quasi-cleavage mechanism

with 3,000 psi H_2



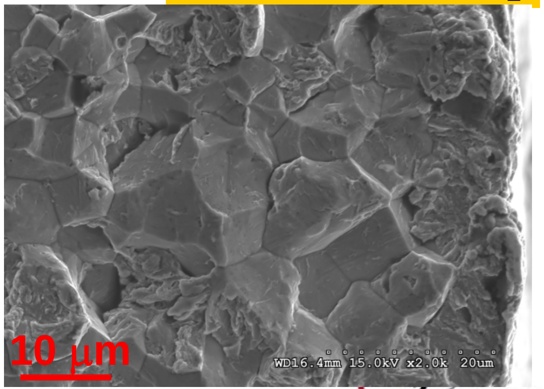
- **Brittle intergranular fracture**
  - Devastating hydrogen effect
  - Promoted by hydrogen induced decohesion at interfaces

High-strength 4340 steel
Intergranular failure

Hydrogen-free

•Indentification of the fracture mechanism
•Statistical model of fracture
•Weakest link statistics
•Strength prediction

with 20,000 psi H_2



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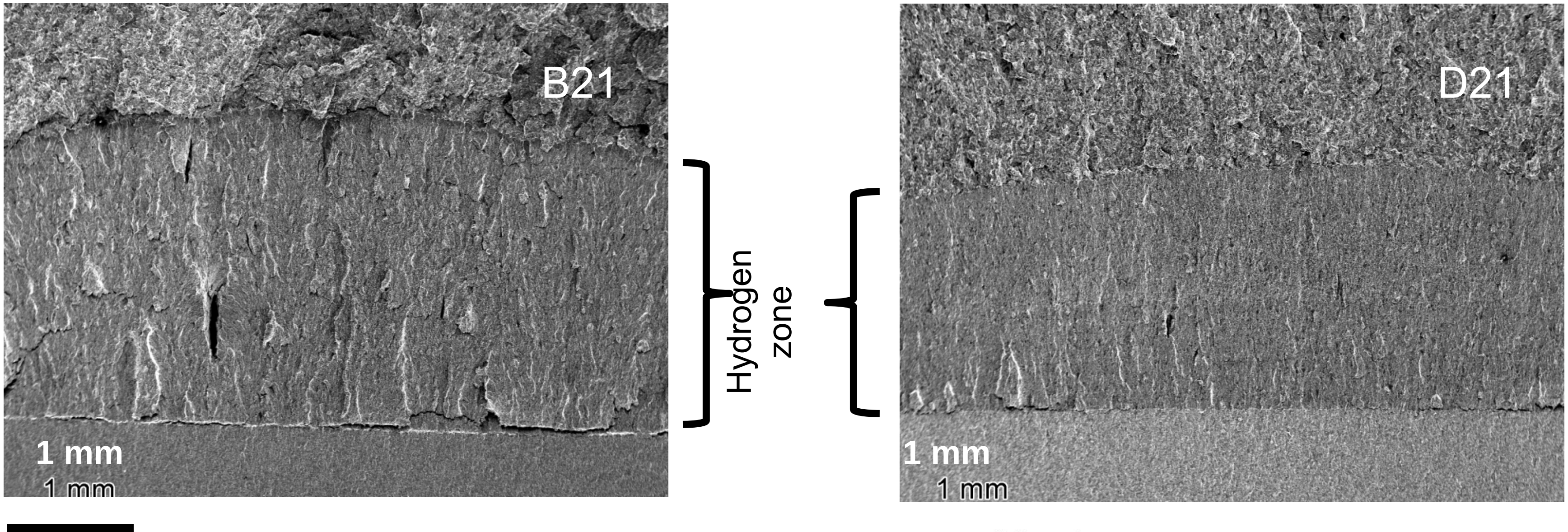
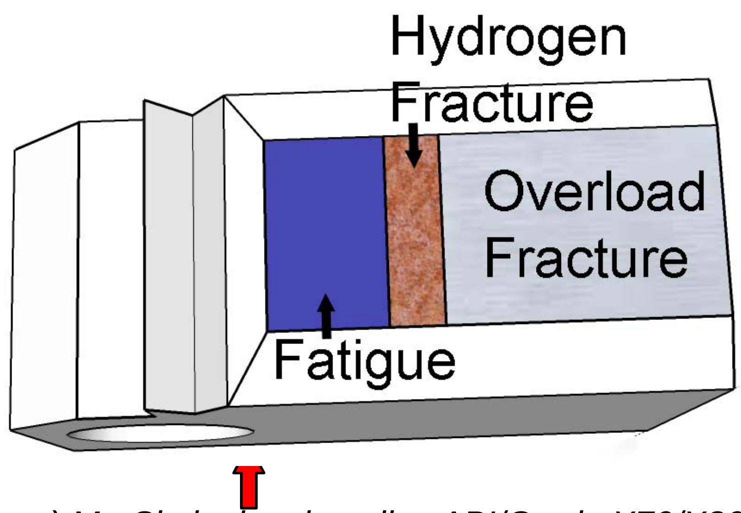
New Pipeline Steel Microstructures
SEM View of Specimens B and D Fractured in 3 ksi H2 gas



Images taken at Sandia

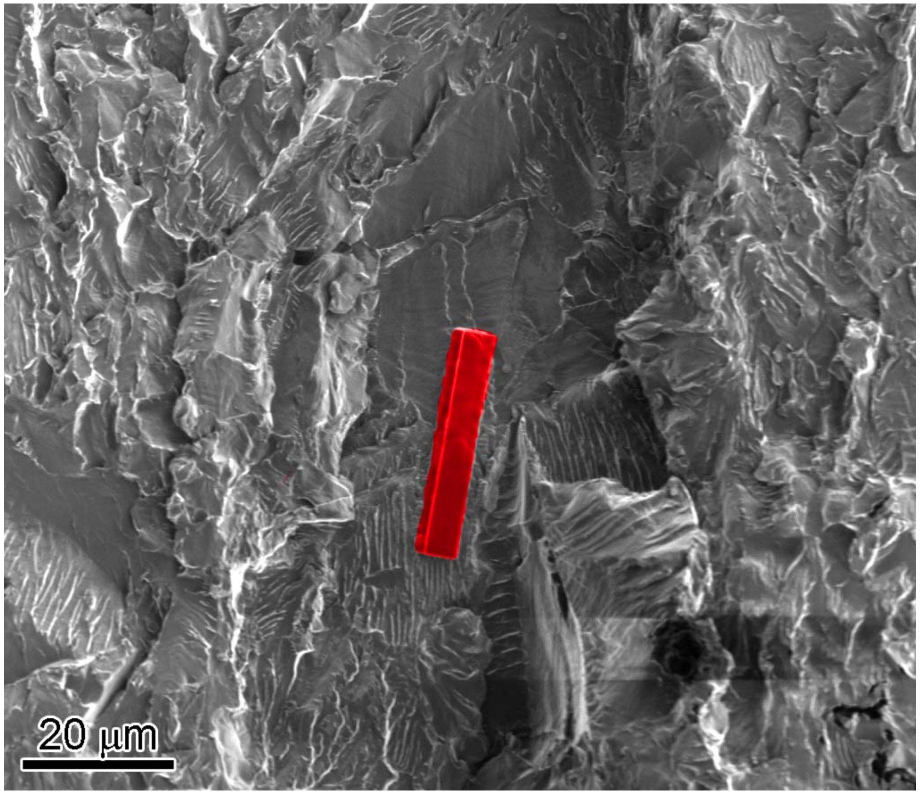
- Compact tension specimens tested in hydrogen environment at Sandia National Laboratories
- Area of fracture easily identified in SEM
- Identify features of interest



- *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*

Hydrogen-induced Fracture Morphology: Quasi-Cleavage

We identified feathery and featureless flat areas to locate our FIB sample area of interest

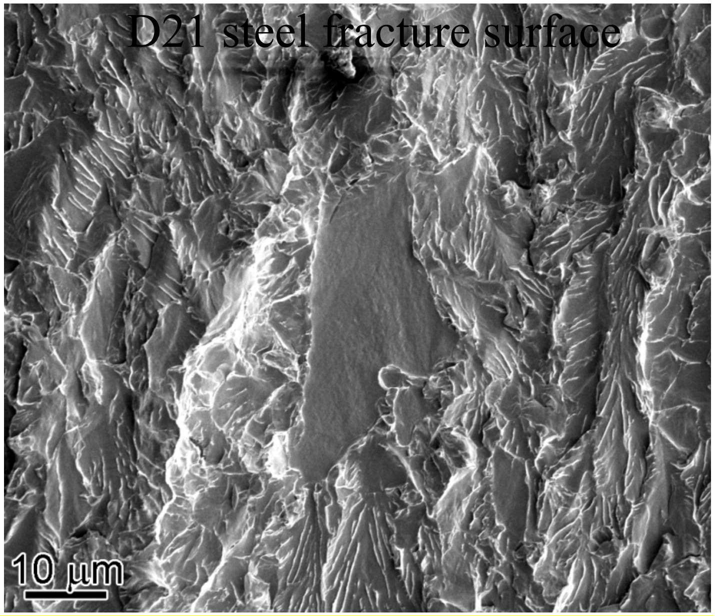


Need to understand how these morphologies relate to microstructure and hydrogen effects on it.

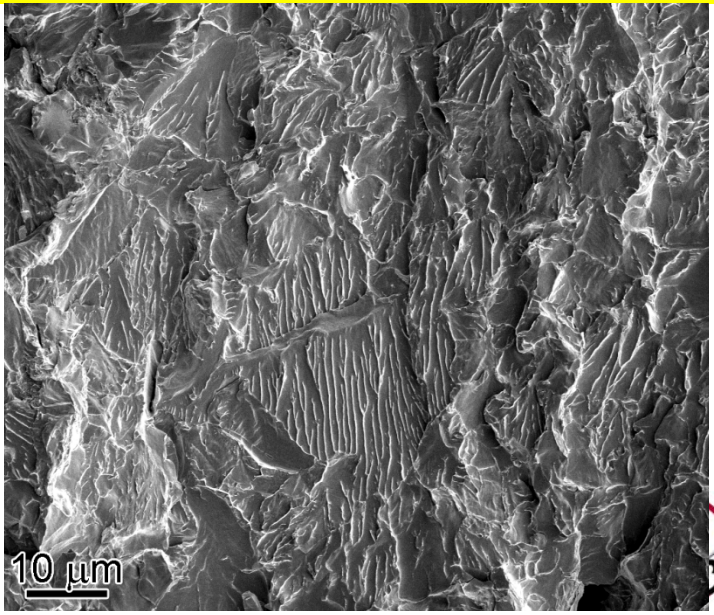
Two approaches used:
- High-resolution SEM + 3D visualization
- TEM of just beneath the fracture surface.

Closer view of the two different morphologies

D21 steel fracture surface



What is Quasi-Cleavage?



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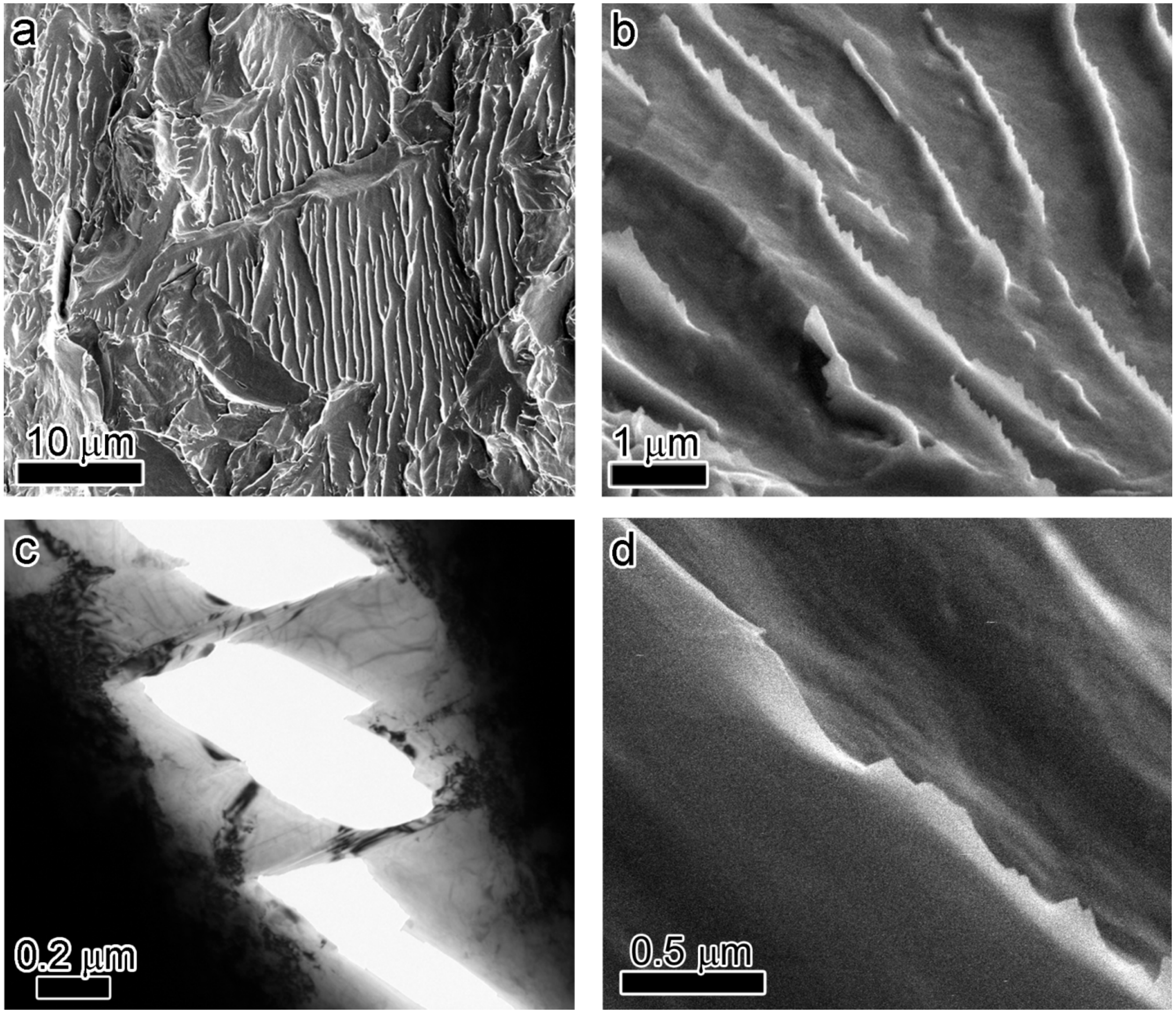
Unique Features Identified on Fracture Surface



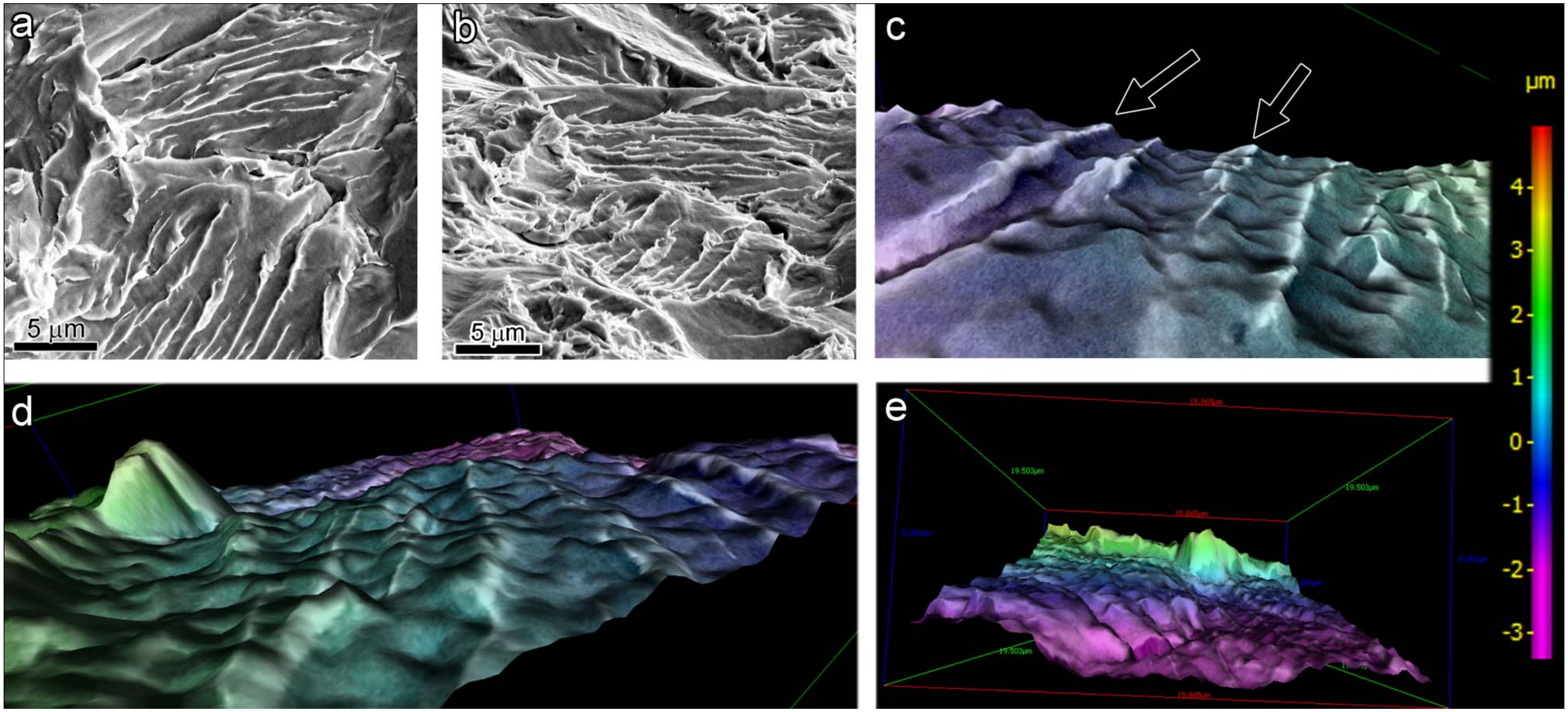
TEM image of in-situ fractured Cu-3%Co sample showing saw-teeth due to final tearing. Image courtesy of G. Liu.

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.

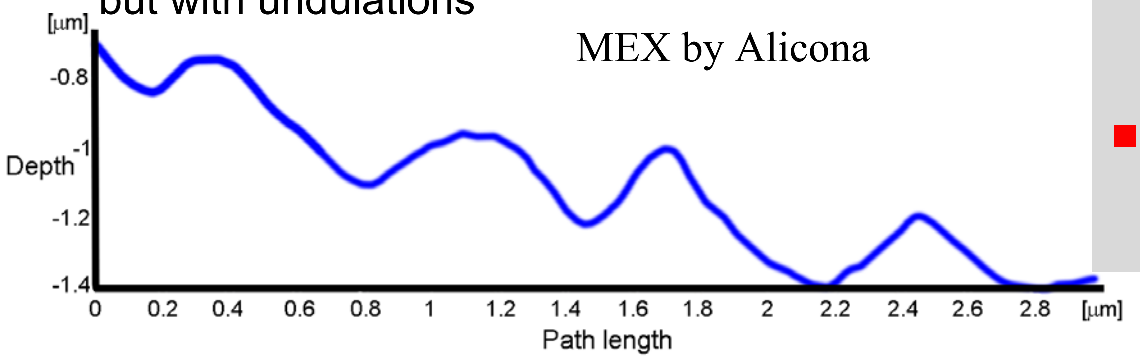
The mechanism of formation of the saw-teeth in the TEM sample is understood.

The presence of the ridges suggests plastic processes (final separation), but how are they related to hydrogen and the fracture mechanism?

Ridge Surface Topography Confirmed/Revealed by 3D Visualization

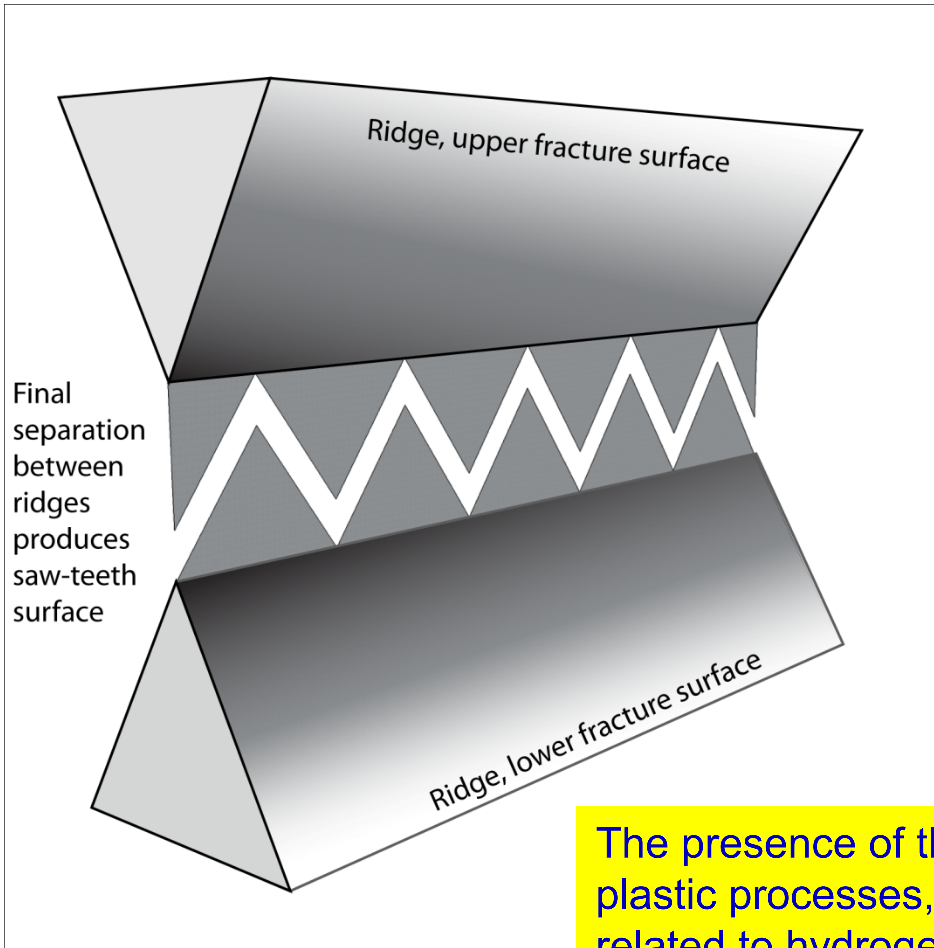


Parallel nature of ridges: area between not smooth but with undulations



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

Fracture Surface: Ridges and Saw-Teeth



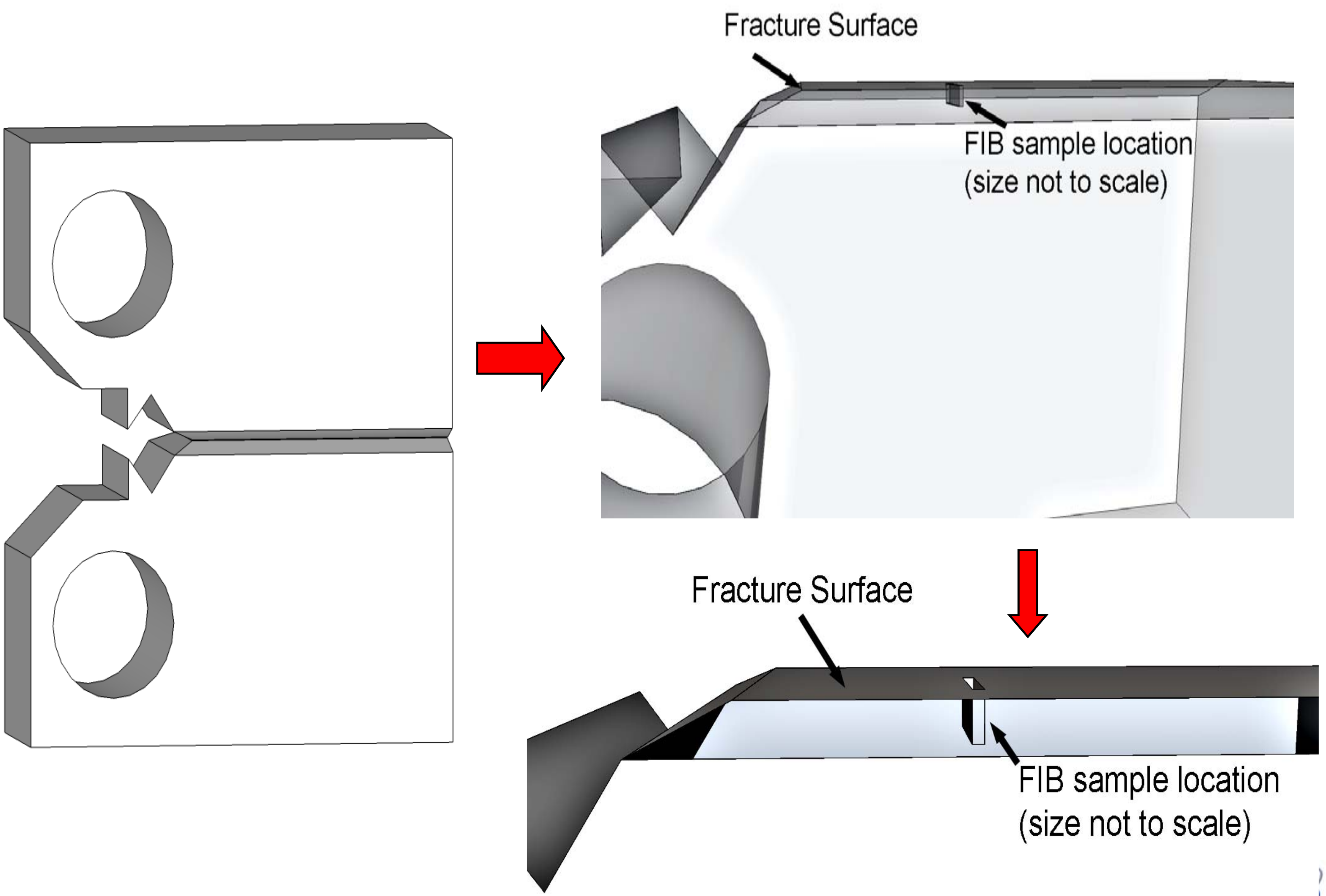
High-resolution SEM image reveals the presence of “saw-teeth” on top of the ridges. These are reminiscent of “saw-teeth” formed on final separation of thin sections in the transmission electron microscope.

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

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

This will answer the question of what Quasi-cleavage is.

Focused Ion Beam (FIB): Sample Orientation

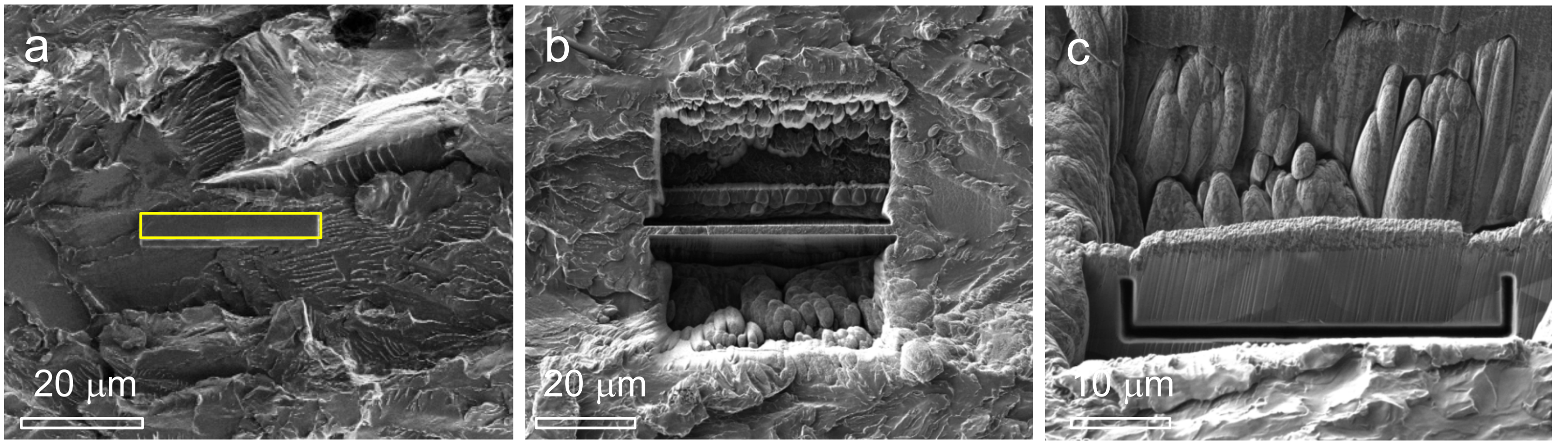


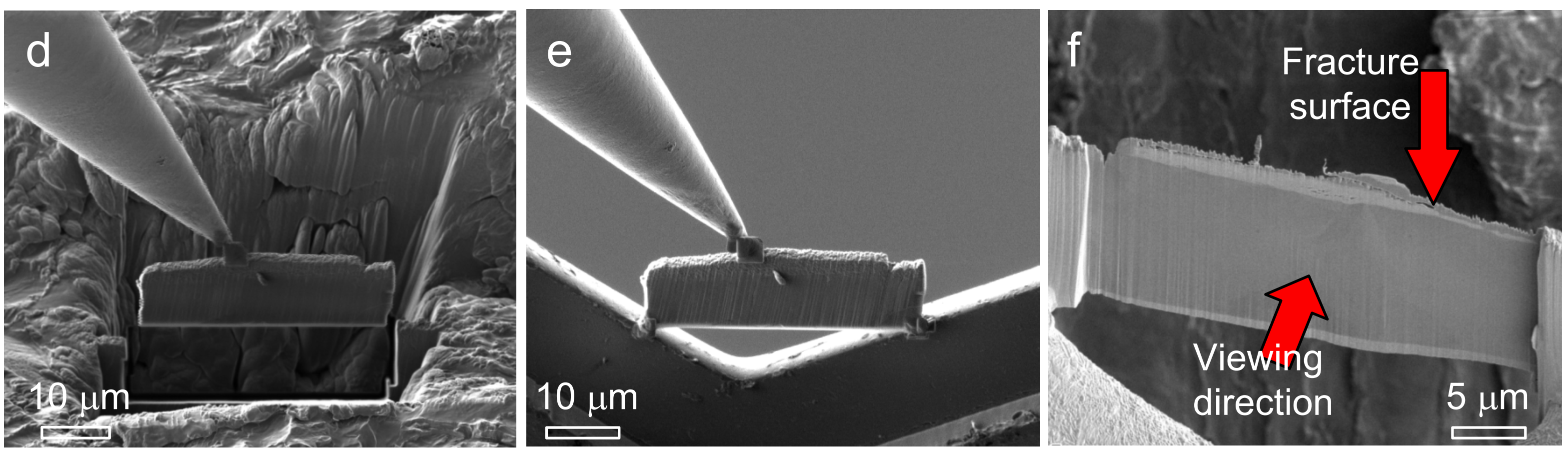
Site Specific Sample Extraction from a Rough Surface using Focused Ion Beam Machining

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.

Cut needle free from sample
Thin to electron microscopy.

Discovery of the Mechanism Responsible for "Quasi-Cleavage" Fracture

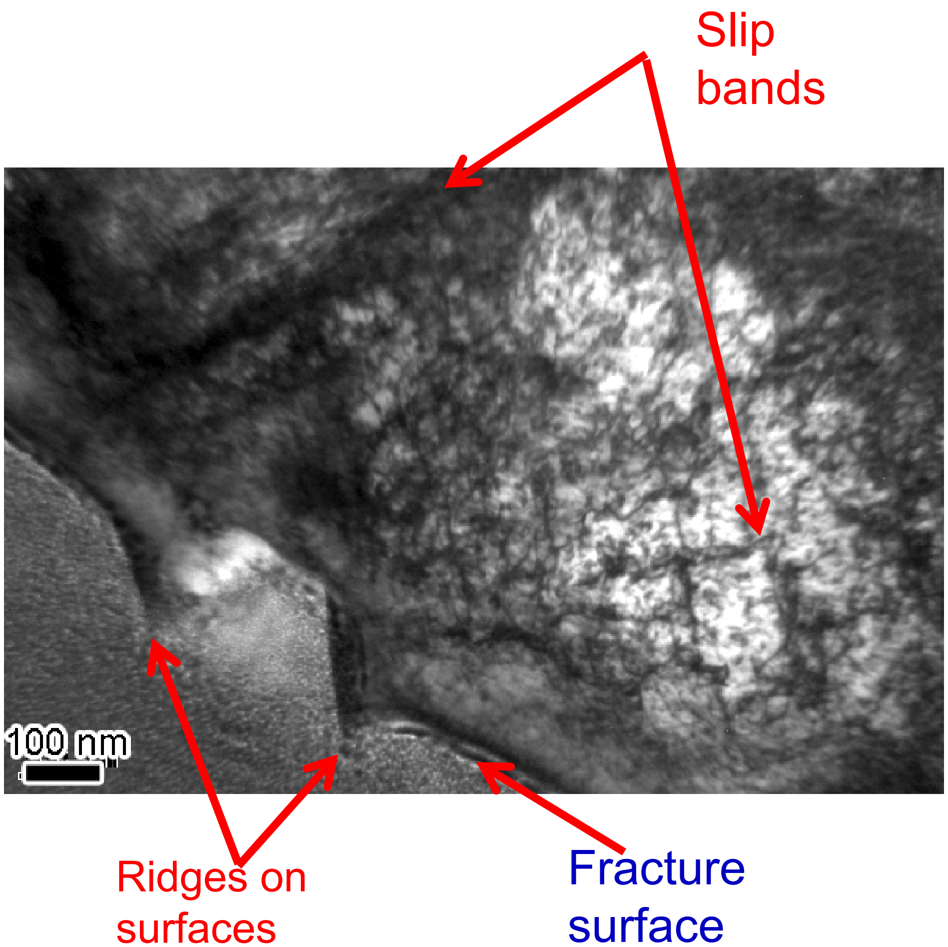


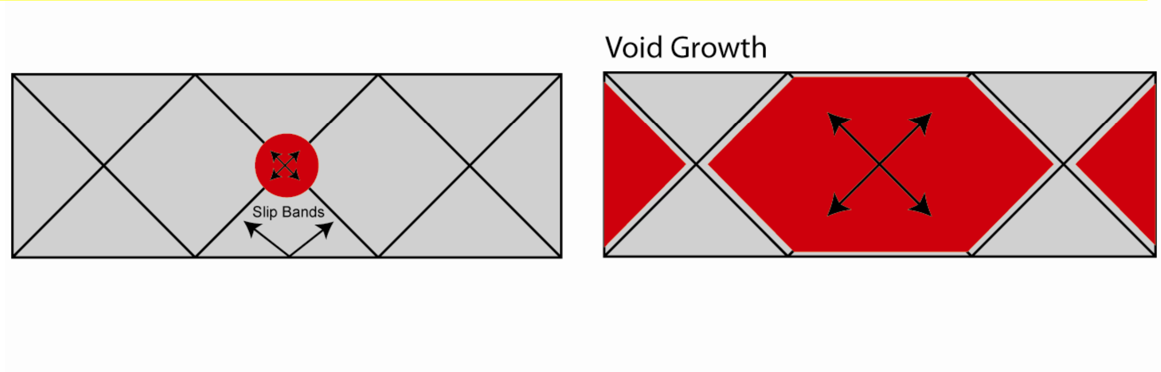
Image shows slip bands parallel to ridge edges, suggesting "quasi-cleavage" is not a cleavage like process but is related to dislocation slip. Enhanced and confined slip activity is consistent with hydrogen enhanced local plasticity mechanism.

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

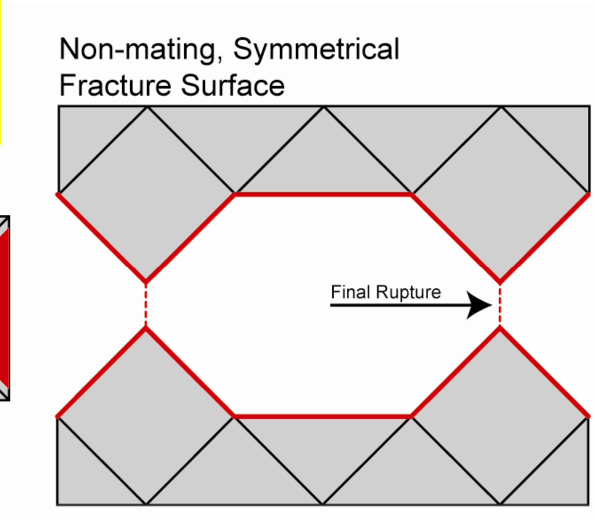
Slip planes densely packed with dislocations

Hydrogen-Induced Fracture Explained

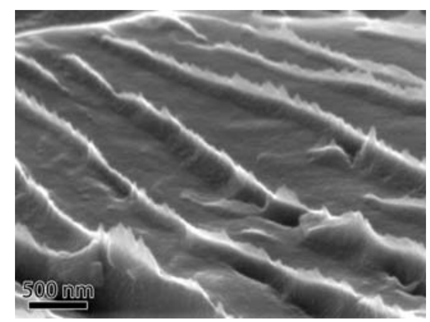
Hydrogen-induced void nucleation and growth at slip band intersections



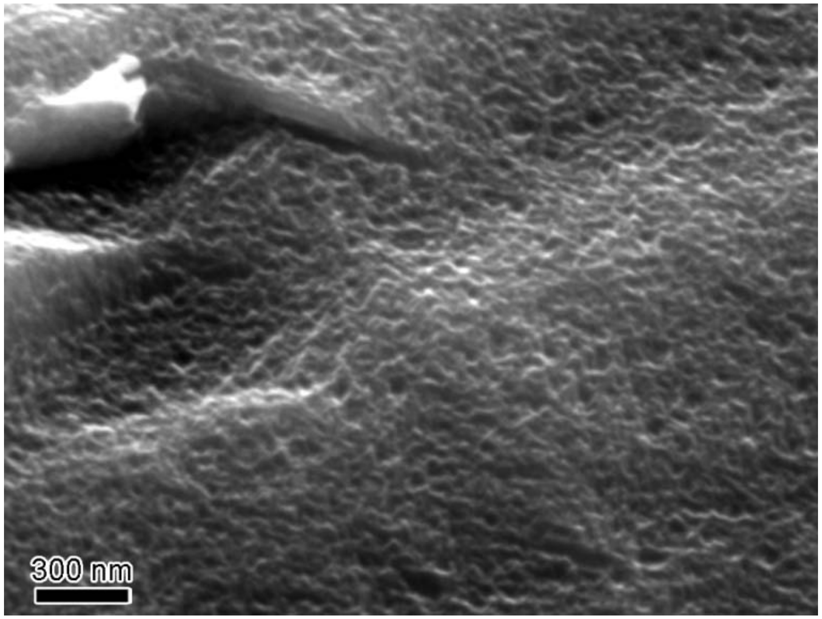
Matching surfaces

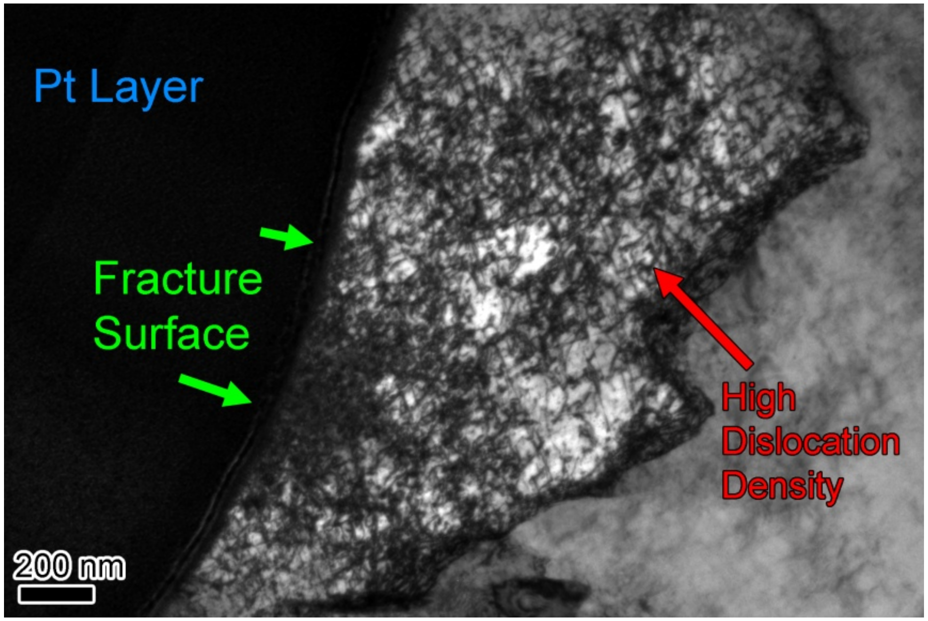


- **Voids open up at intersection of slip bands**
  - **Open along lines of intersection forming tubes**
- **Voids expand by dislocation processes until they encounter another void**
- **Final failure along tops of ridges forming saw-teeth**



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**

Analysis of Cracked Pipeline
Hydrogen-Deformation Interactions

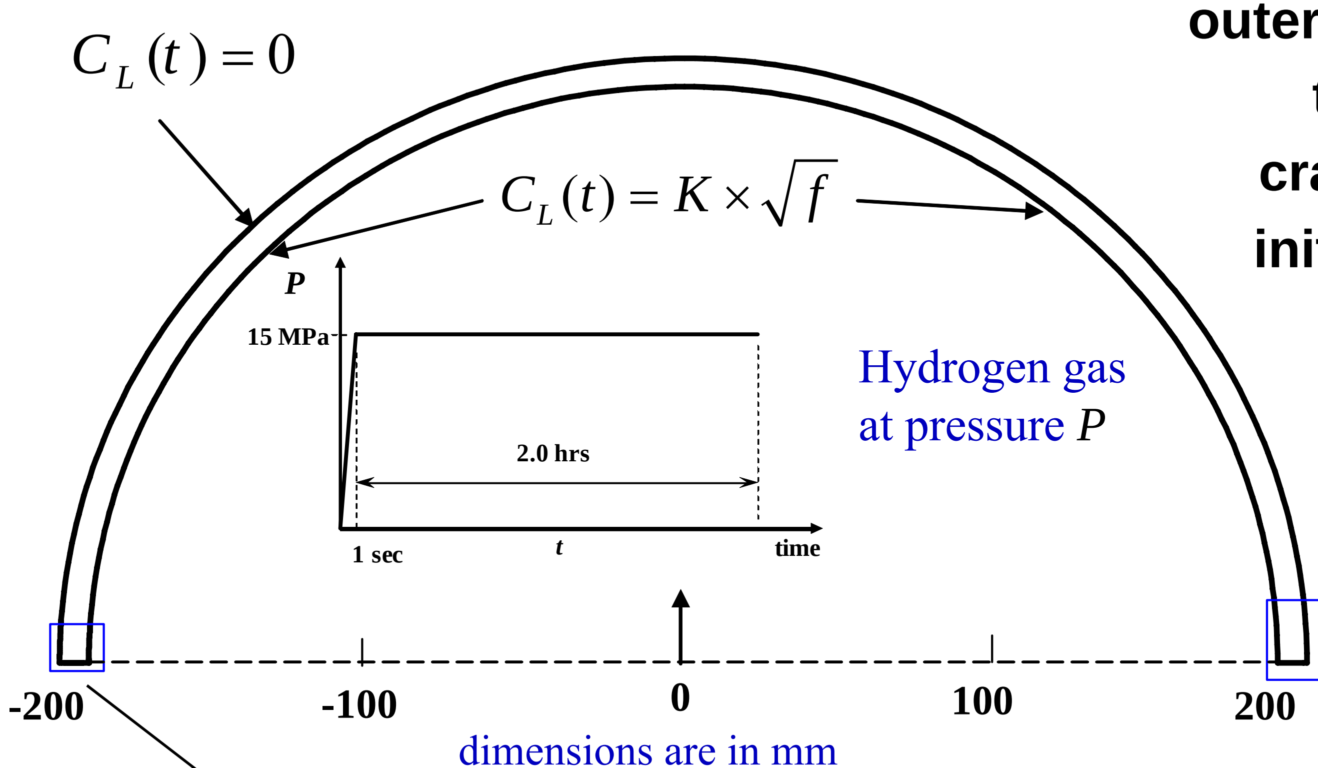
outer diameter: 40.64 cm

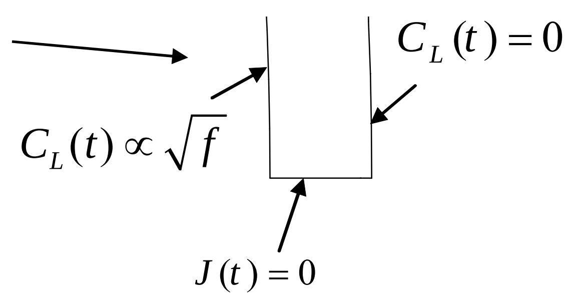
thickness: $h = 9.52$ mm

crack depth: $a = 1.9$ mm

initial CTOD: $b_0 = 1.5$ µm

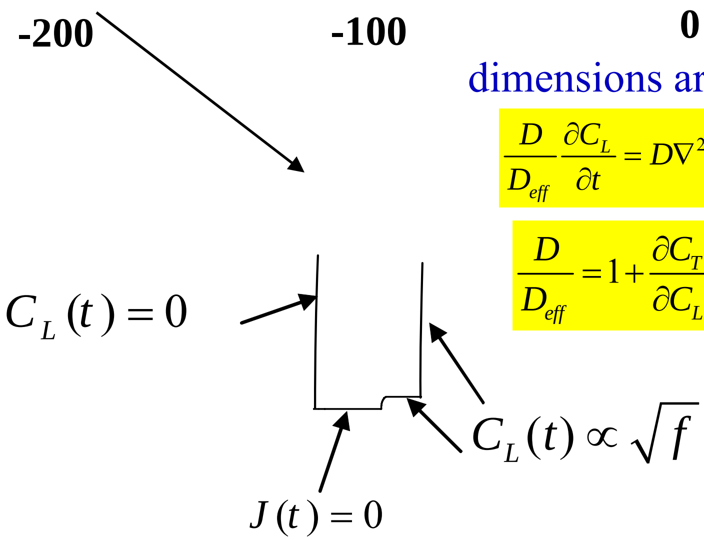
$a / h = 0.2$

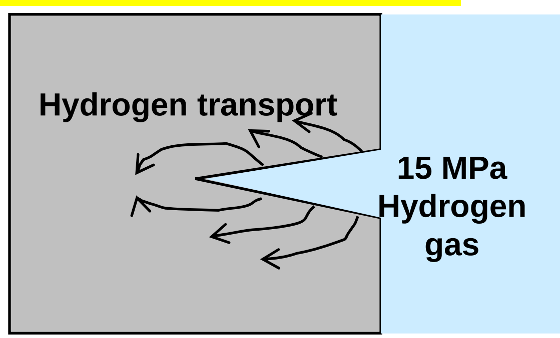




$$\frac{D}{D_{eff}}\frac{\partial C_L}{\partial t} = D\nabla^2 C_L - \nabla.\left(\frac{D C_L V_H}{3RT}\nabla\sigma_{kk}\right) - \alpha\theta_T \frac{\partial N_T}{\partial \varepsilon^p}\frac{d\varepsilon^p}{dt}$$

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





K : **Solubility**

J : **Hydrogen flux**

P : **Pressure**

f : **Fugacity**

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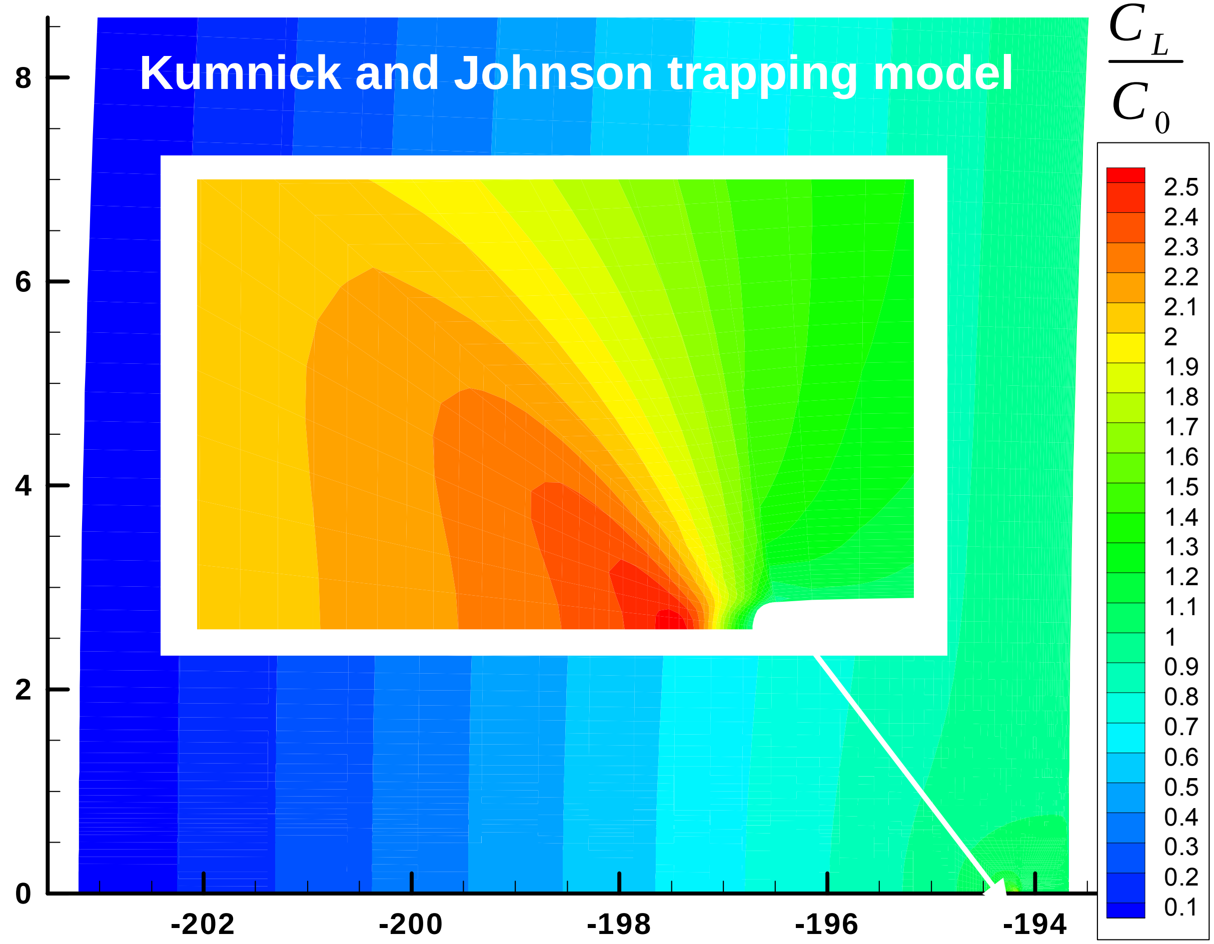
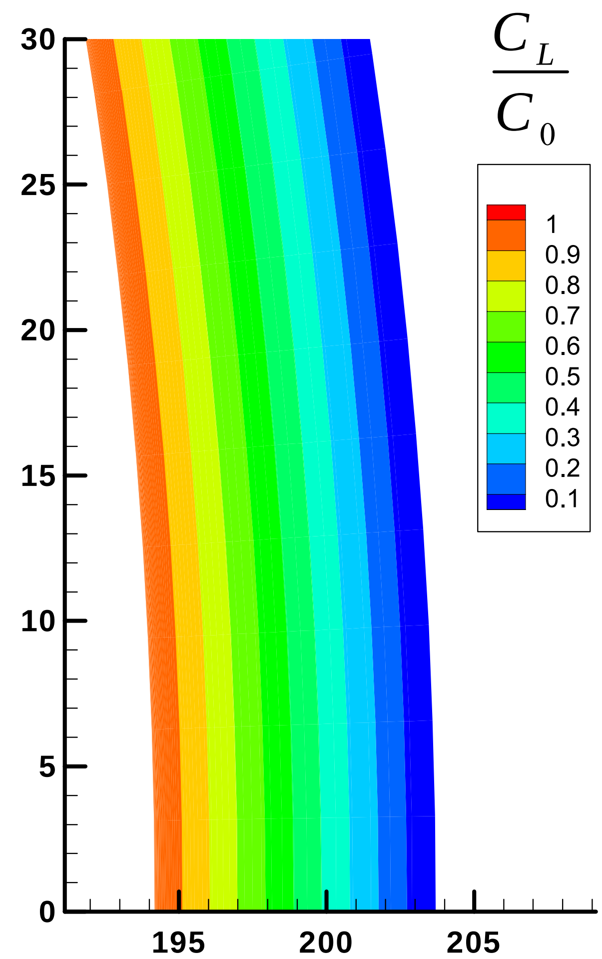
Hydrogen Concentration at Steady-State

Time to steady-state: 2.0 hr





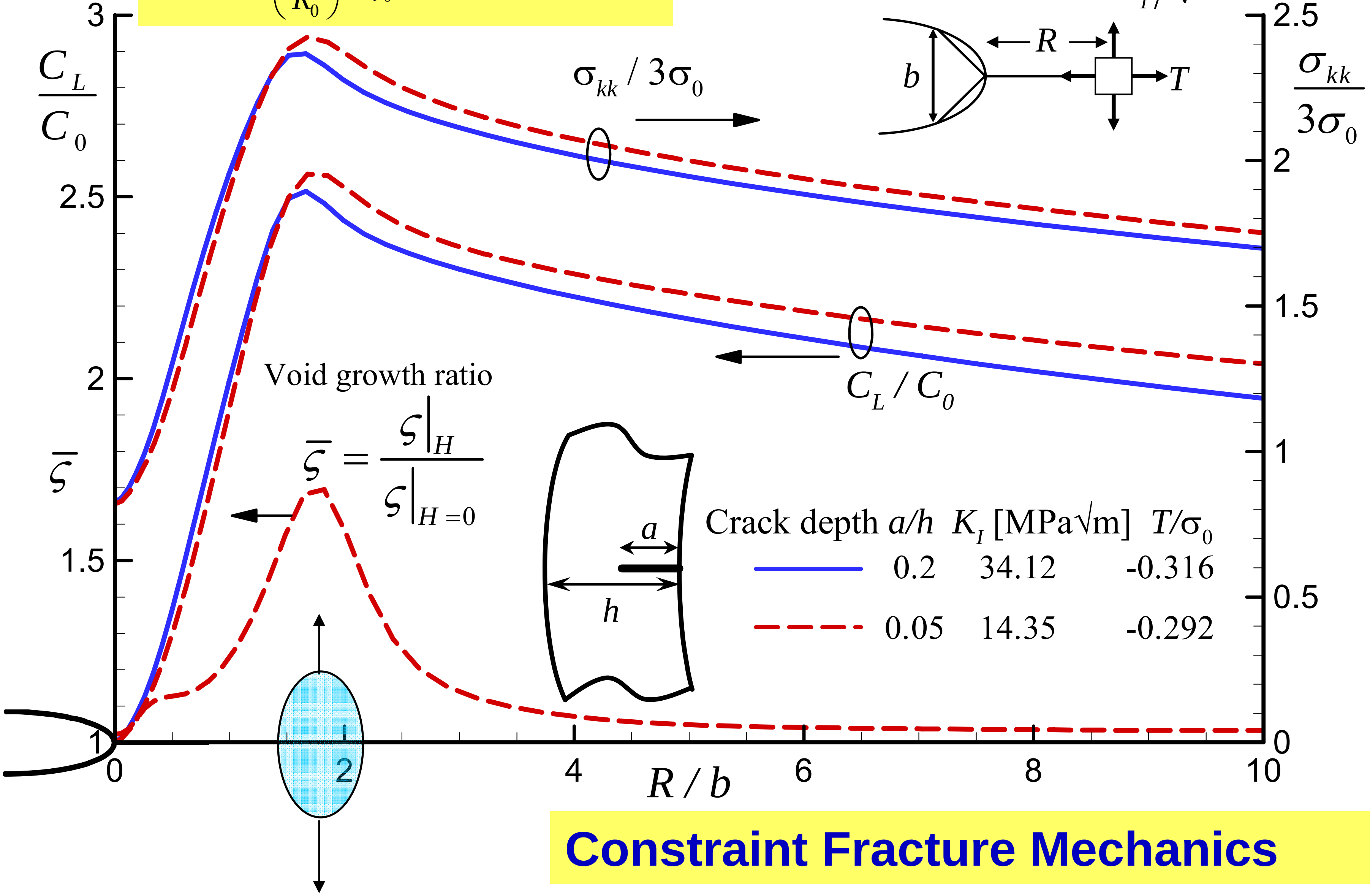
$C_0 = 2.65932 \times 10^{22}$ H atom / m^3

corresponds to lattice concentration at

$P = 15$ MPa

Crack-Tip Fields Scale with K_I and T-stress
Hydrogen Accelerates Void Growth

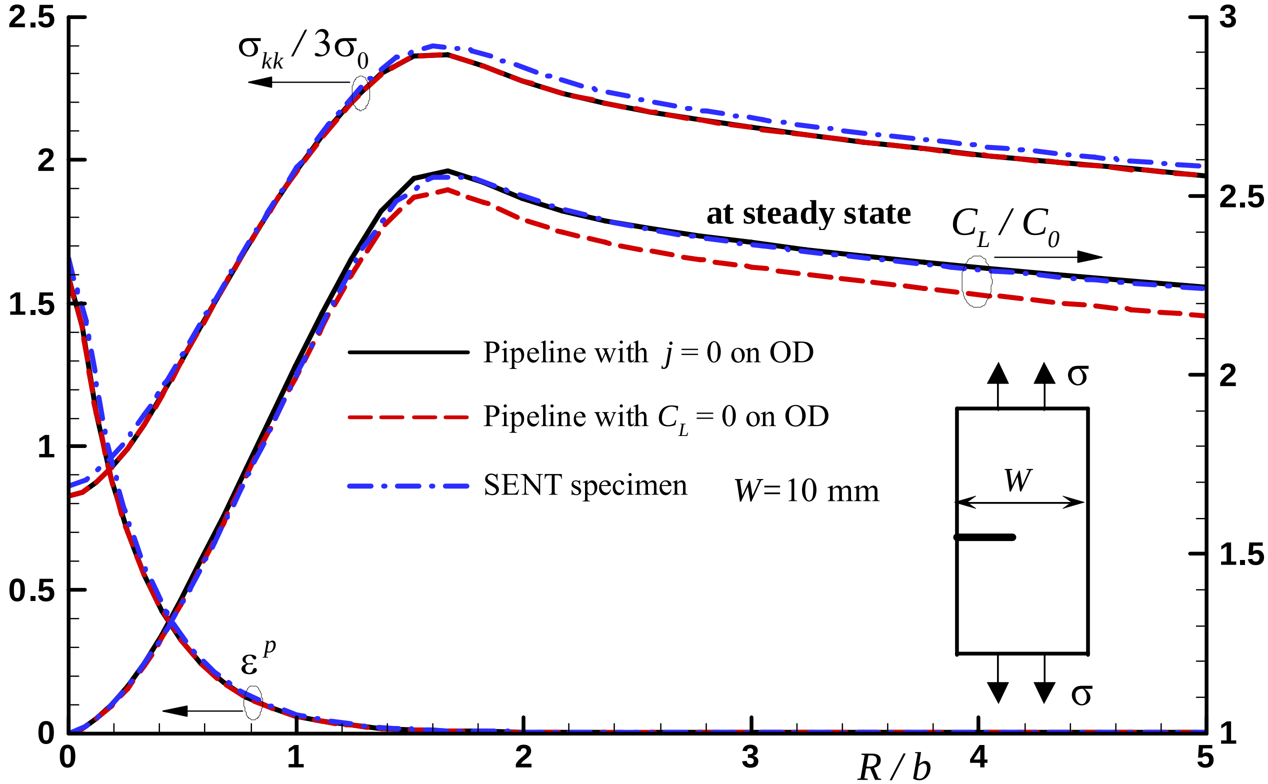
$$\varsigma(\varepsilon^p) = \ln\left(\frac{R_v}{R_0}\right) = \int_0^{\varepsilon^p} a_v \exp\left(\sigma_{kk}/\sigma_Y\right) d\varepsilon^p$$

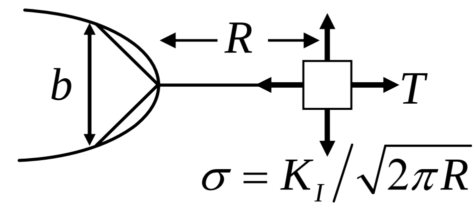


Constraint Fracture Mechanics

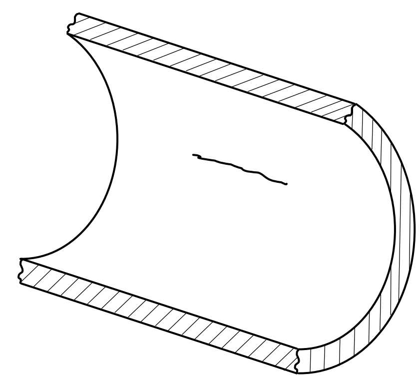
From the Pipeline to the Laboratory Specimen
Environmental Similitude with Single Edge Notch Tension

Constraint fracture mechanics





Cracked-Pipeline Fields vs. SENT-Specimen Fields

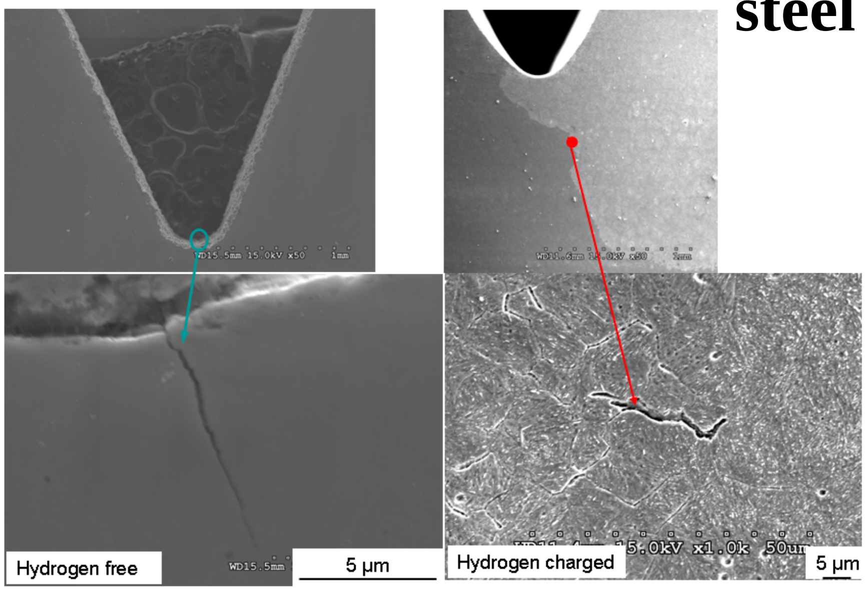


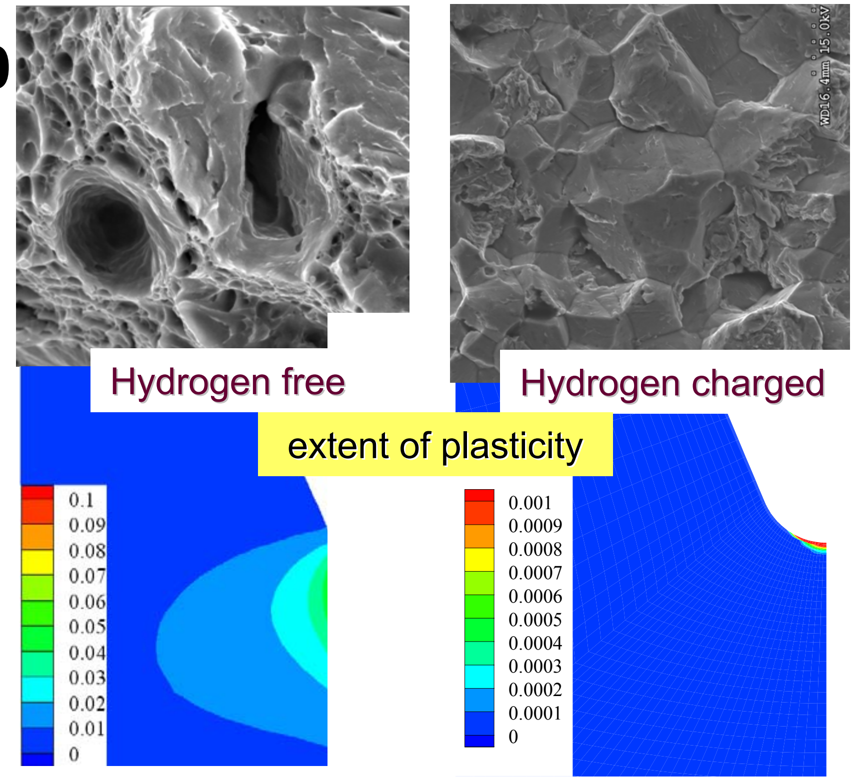
- Pipeline fields scale with the stress intensity factor and *T*-stress at the axial crack.
- Single Edge Notch Tension (SENT) specimens can be used to study fracture resistance of a pipeline with an axial crack

Intergranular Failure of High Strength Steels
Identification of the Fracture Mechanisms

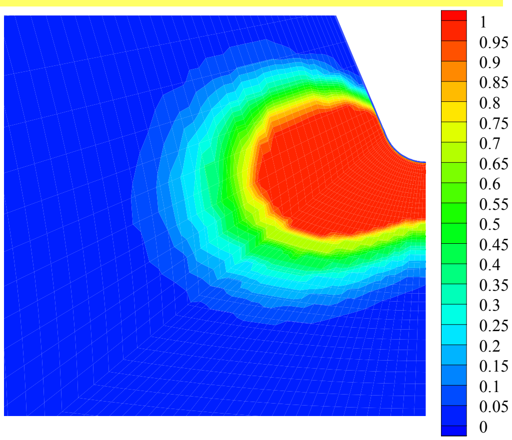
Statistical microstructure to macroscale modeling

AISI 4340 steel





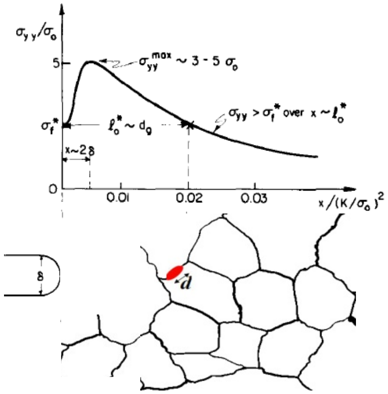
computed failure probability



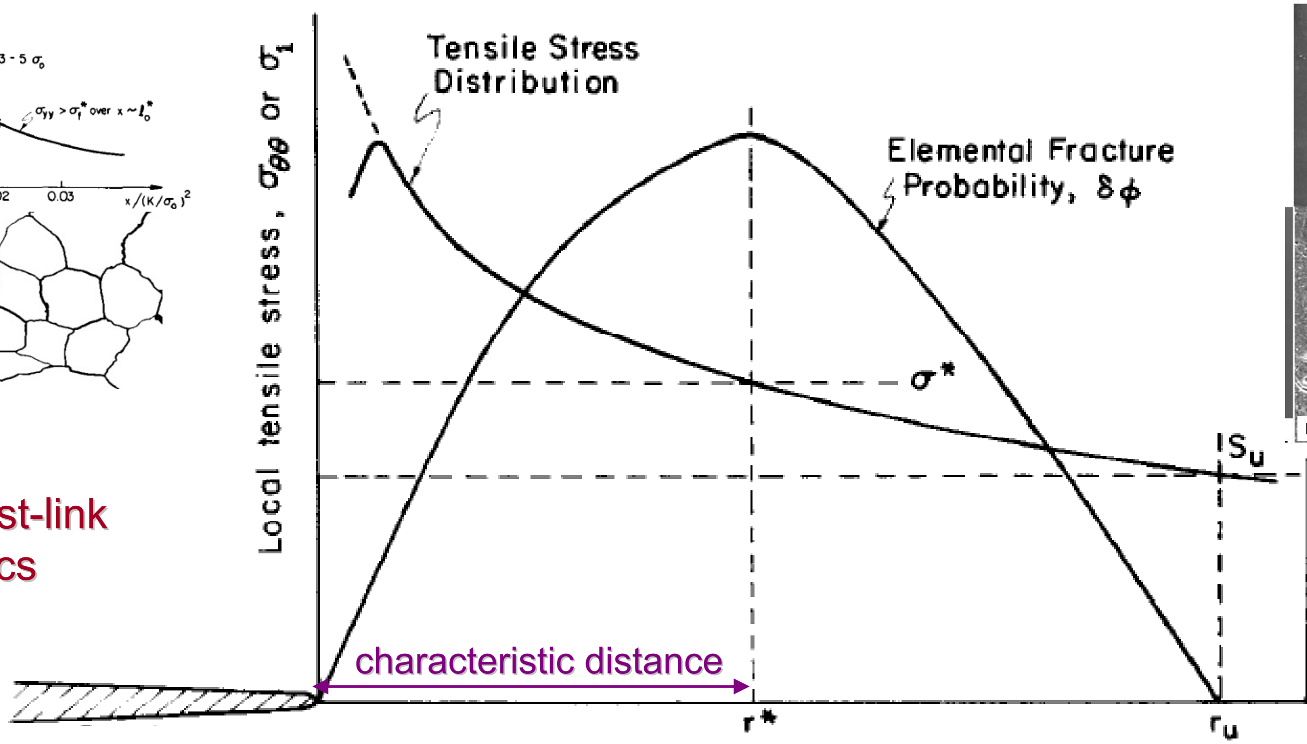
- experiment and theory show that whereas *ductile fracture* is locally *strain-controlled*, *H-induced brittle intergranular fracture* is locally *stress-controlled*
- statistical model (RKR adaptation) predicts location of the highest probability of failure ahead of the notch root
- ***failure predicted on the basis of weakest-link decohesion fractures in critical boundaries***

Statistical Model of Hydrogen Induced Fracture

Critical event identified as H-induced interfacial failure at grain boundary carbides

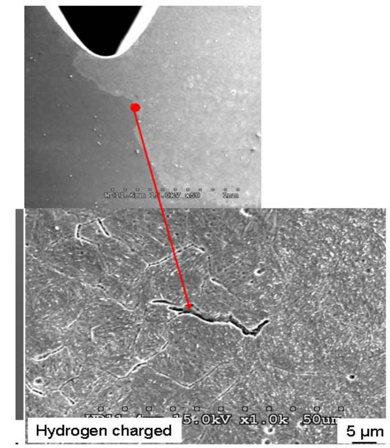


using weakest-link statistics



Crack or notch

Distance ahead of crack or notch tip, r



Φ = failure probability of structure

A weakest-link statistics model requires

- Stress distribution around the crack or notch
- Distribution of matrix/carbide interface strengths which are directly related to the local hydrogen amount

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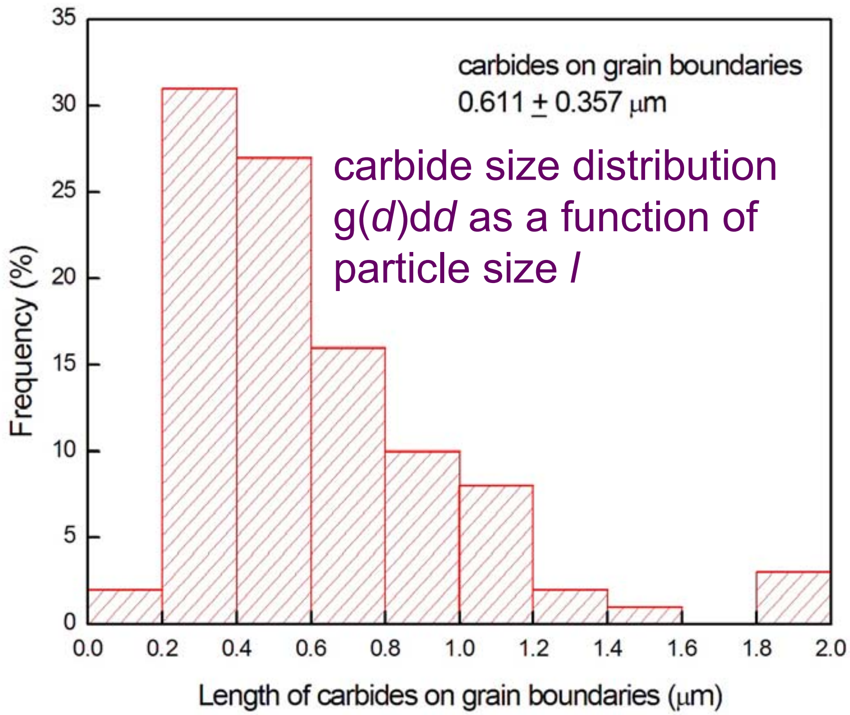
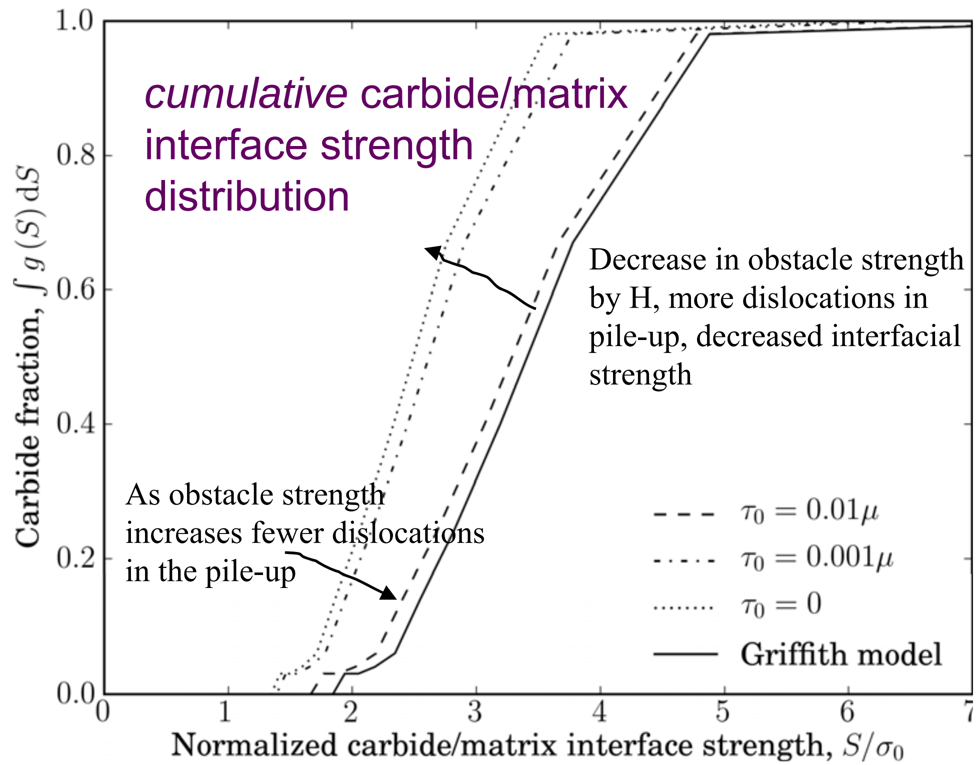
Statistical Model of Hydrogen Induced Fracture

AISI 4340 high-strength steel





Use Smith model of fracture to determine the carbide/particle interface distribution from the carbide size distribution

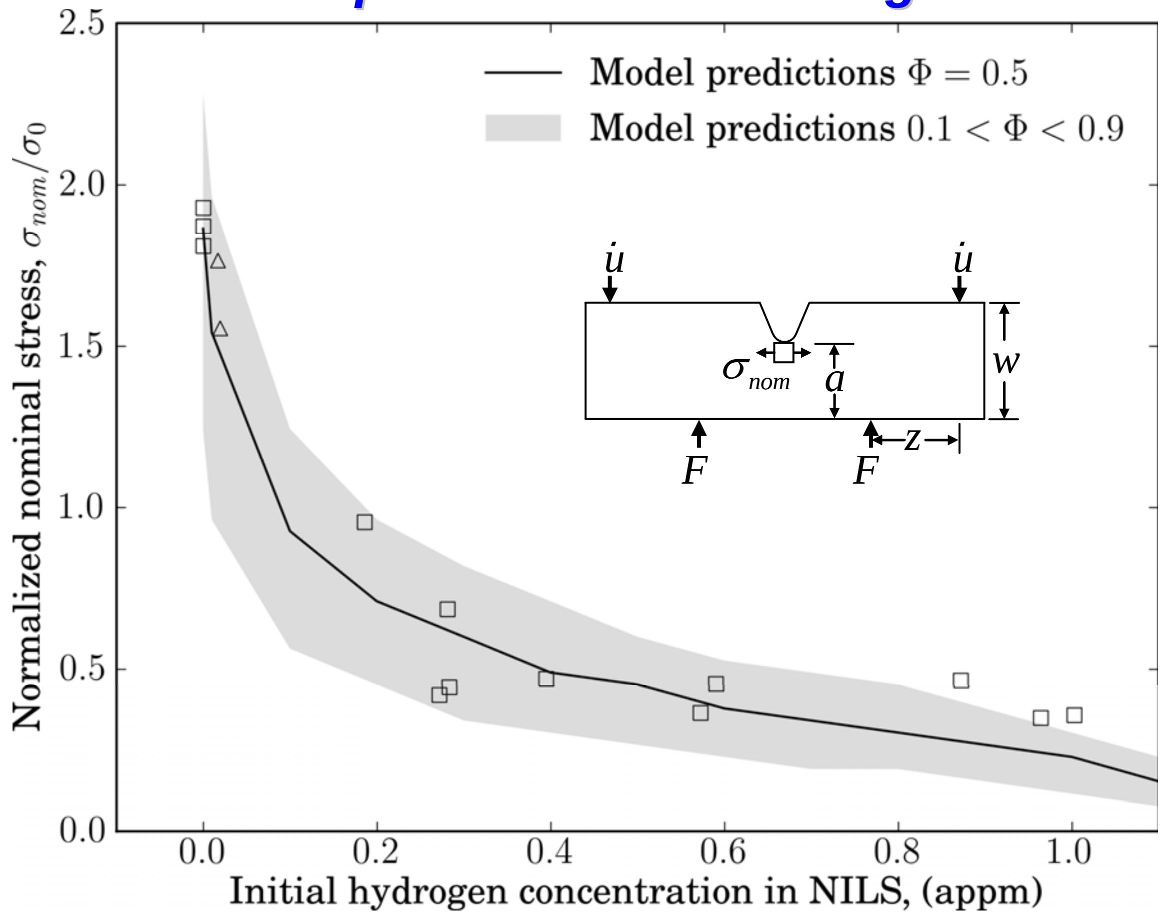
$$\frac{l}{d}S^2 + \tau_{eff}^2\left[1+\frac{4}{\pi}\frac{\tau_0}{\tau_{eff}}\sqrt{\frac{l}{d}}\right]^2 = \frac{4E\gamma_{eff}}{\pi(1-\nu^2)d}$$

E: Young's modulus
ν: Poisson's ratio
l : carbide size
γ_{eff} : effective fracture work

Critical Stress for Hydrogen-Induced Fracture

Results for four-point bend single edge notched specimens

Experiment vs. Modeling



This model permits the prediction of the statistical degradation in strength of a material as a function of the concentration of hydrogen

Expected Accomplishments

- Hydrogen-embrittlement resistant materials for the design of a safe and reliable hydrogen infrastructure
- Efficient and scalable hydrogen production through artificial photosynthesis
- Novel hydrogen storage materials (over 6wt% H_2 system capacity)
- Next generation efficient fuel cells through novel materials and devices
- New material transformation processes (catalytic oxidation) with no CO_2 and waste energy by-products
- Low cost/energy CO_2 separation and concentration processes
- Scientific evaluation of CO_2 storage and geological or sub-seabed sequestration
  - Society decisions based on sound scientific information

Acknowledgments

- US Department of Energy
- NSF
- University of Illinois at Urbana-Champaign
  - I. Roberston, M. Martin, M. Dadfarnia, P. Novak
- Sandia National Laboratories, Livermore
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- University of California, Berkeley
  - R. Ritchie, R. Yuan
- Kyushu University
  - Y. Murakami, T. Kanezaki
- DGS Metallurgical Solutions, Inc.
  - D. Stalheim

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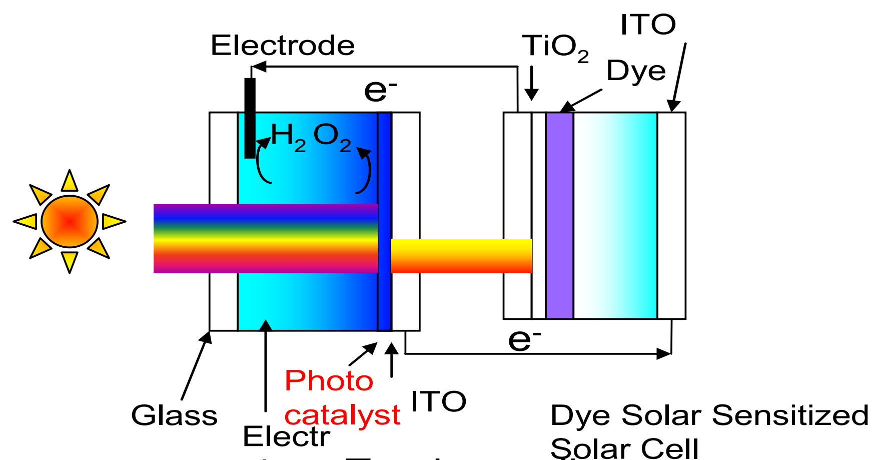
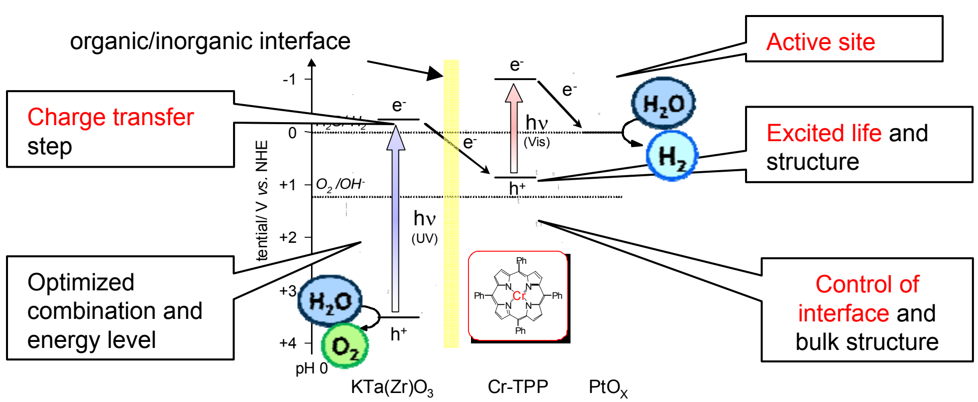
Hydrogen Production by Artificial Photosynthesis

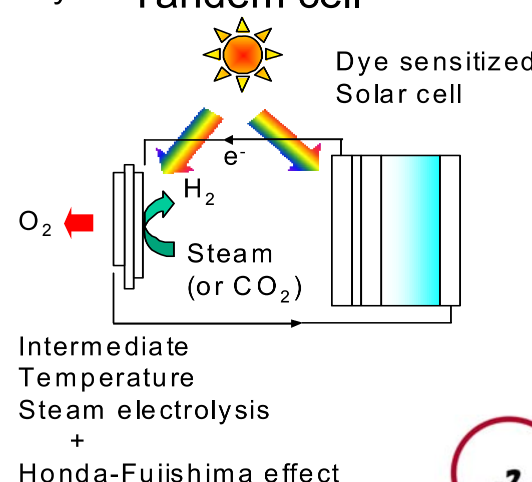
- **Roadblocks**
  - H_2 formation by complete photocatalytic water splitting proceeds at slow rate and low efficiency due to short lifetime of separated charge
- **Goals**
  - Production of H_2 without forming CO_2 based on photosynthesis type catalysis and new H_2O electrolysis photoreactor
- **Technical approach**
  - Control of interfacial structure of semiconductor
  - Understand charge transfer from semiconductors
  - Determination of photo-excited state life
  - Development of an efficient catalyst and electrolyzer



Tandem cell



Photocatalyst

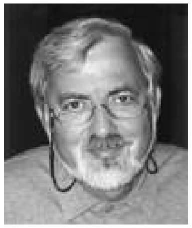


Steam electrolysis with DSS

Next Generation Fuel Cells

- **Roadblocks**
  - Limited application conditions of fuel cells due to limited operational range of electrolyte and electrode materials
- **Goals**
  - Understand fundamentals of chemistry and electrochemistry of solids for advanced fuel cells, at chemical defect, crystallographic and nano-structural levels, at material interfaces, and in nano-regions
- **Technical approach**
  - Elucidate the nano-level reaction mechanisms
    - electrons, atoms and molecules in fuel cells
  - Next generation fuel cells
    - New materials (electrocatalysts, electrolytes, and electrode assemblies)
    - New fuel cell concepts (alternative cell designs or approaches)

K. Sasaki

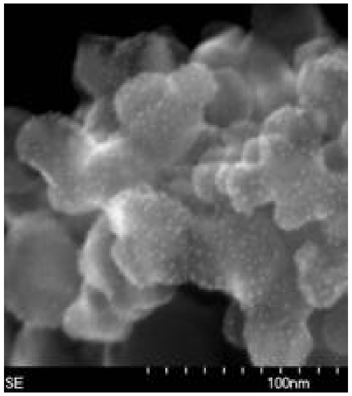


L.J. Gauckler

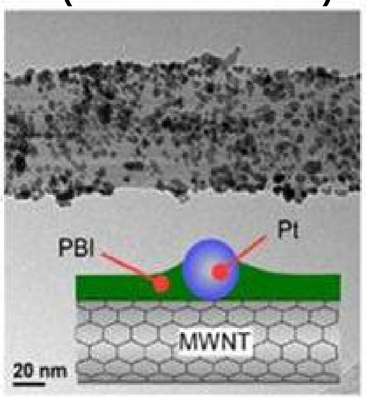
N. Nakashima

H. L. Tuller

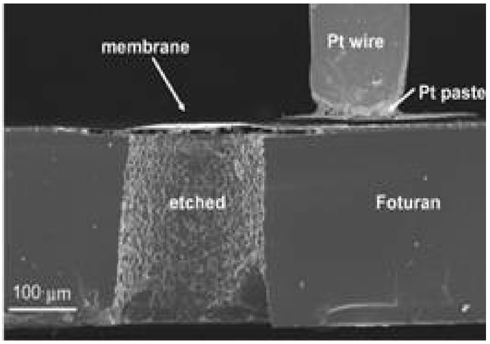
Carbon-free fuel cell electrocatalysts (Prof. Sasaki)



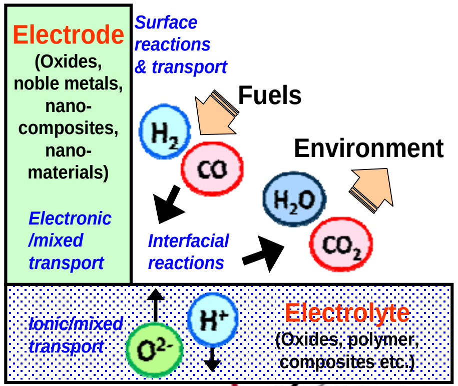
Carbon-nanotube supported fuel cell electrocatalysts (Prof. Nakashima)



Micro fuel cells on Si-technologies (Prof. Gauckler)



Interfaces and fundamental processes in fuel cells



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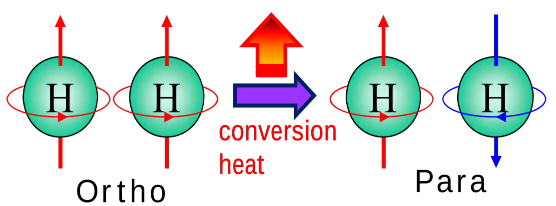
Thermophysical Properties of H_2 and CO_2

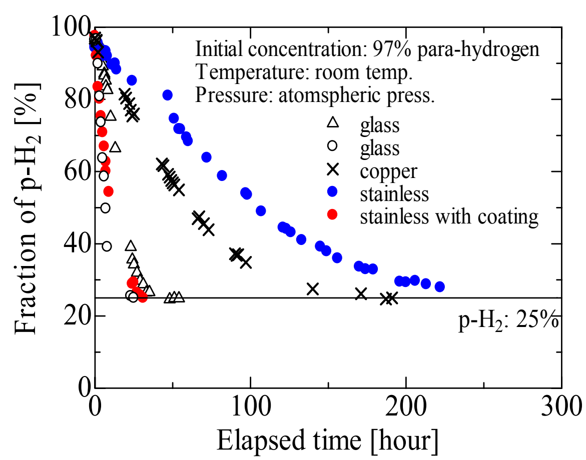
- **Roadblocks**
  - Thermophysical properties of hydrogen and CO_2 at ultra high pressures are not thoroughly available
- **Goals**
  - Understand heat and fluid flow characteristics of hydrogen and CO_2 at ultra high pressures
- **Technical approach**
  - Development of reliable measurement methods for thermophysical properties and heat transfer characteristics of hydrogen at high pressures
  - Elucidation of ortho-para conversion rate of hydrogen in various operating conditions

Y. Takata

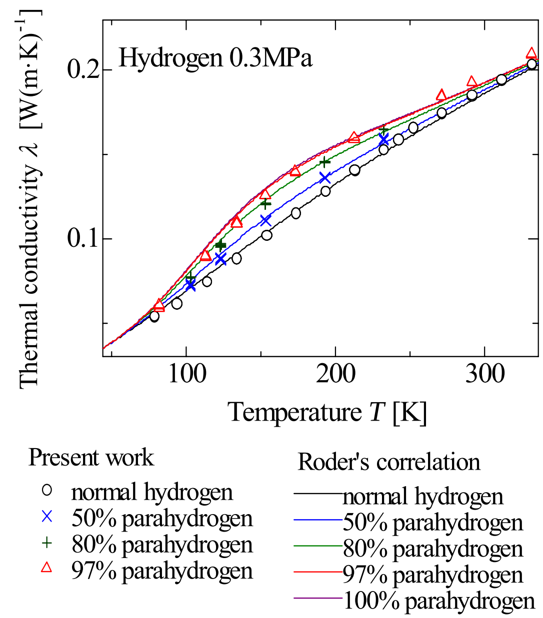
X. Zhang



Conversion between orthohydrogen and parahydrogen in various conditions



Conversion rate from p-H_2 to o-H_2 for various surface materials



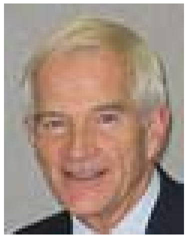
Effect of composition ratio of parahydrogen on thermal conductivity

Hydrogen Storage

- **Roadblocks**
  - Need for efficient method for hydrogen storage, especially suitable for fuel cell vehicles
- **Goals**
  - Design and development of novel hydrogen storage materials at capacities larger than 6 % by weight
- **Technical approach**
  - Devise computational and experimental strategies
  - Understand mechanism and strength of M-H bond
  - Understand hydrogen-surface interactions and diffusion of atoms

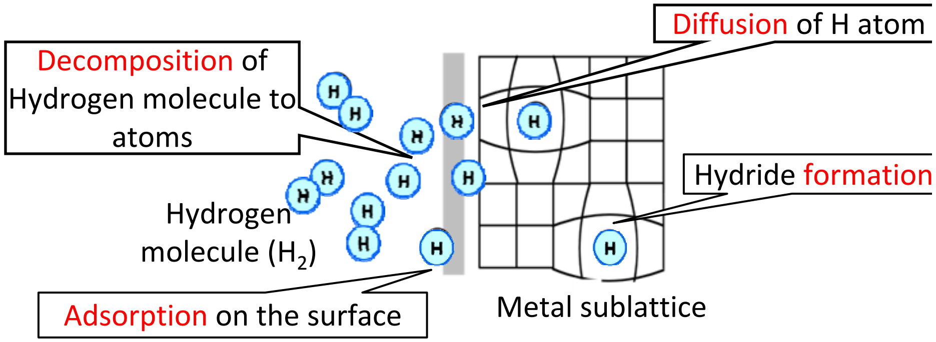
E.Akiba

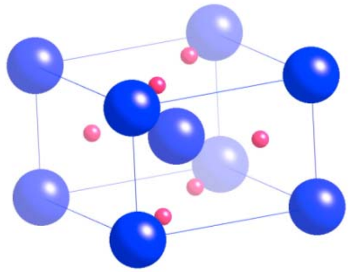
M.Okada



L.Schlapbach

P.Chen





Mg hydride:
One of the candidate materials to be investigated in this Division
Blue: Mg, Pink: Hydrogen

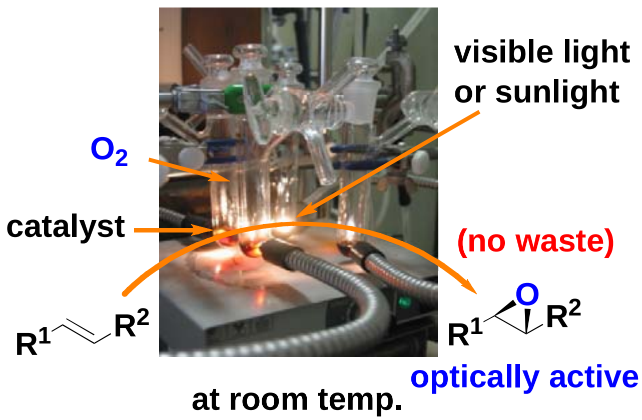
Fuel Cell Vehicle: TOYOTA FCEV
Ti-based hydrogen absorbing alloy that Prof. Akiba and Dr. Iba (TOYOTA) developed was used for on board hydrogen storage.

Advanced Materials Transformation

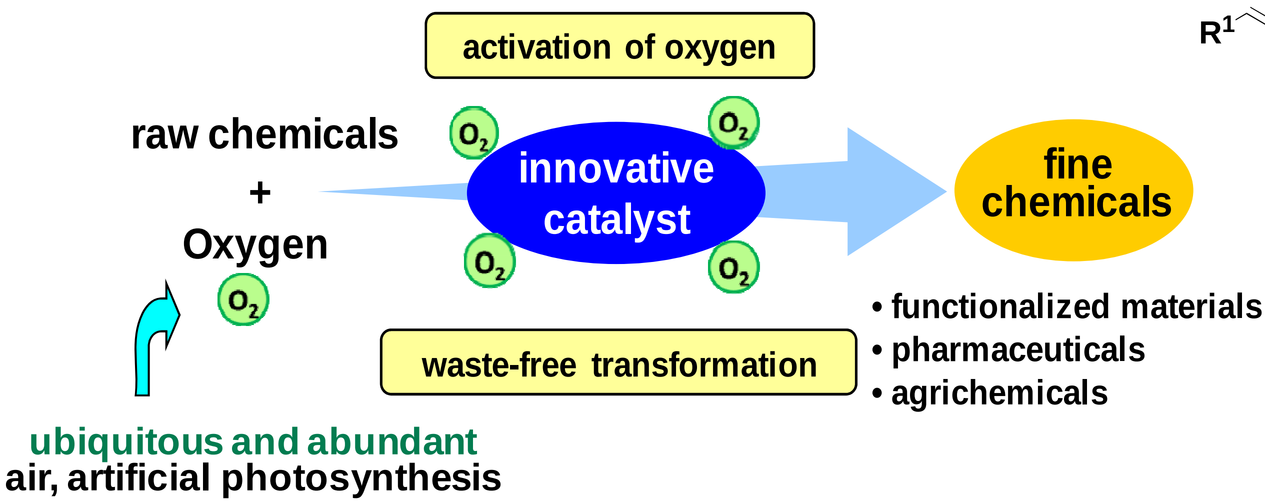
- **Roadblocks**
  - Chemical reactions generate huge amount of waste and CO_2
  - The “green” biological oxidation process is currently impossible to implement with a synthetic catalyst
- **Goals**
  - “Green” the chemical reactions for material transformation (waste-free) by novel asymmetric oxidation catalysts
- **Technical approach**
  - Characterize reaction intermediates in an oxygen activation process
  - Elucidate reaction mechanisms at the molecular level


T.Katsuki


Y.Naruta



aerobic oxidation



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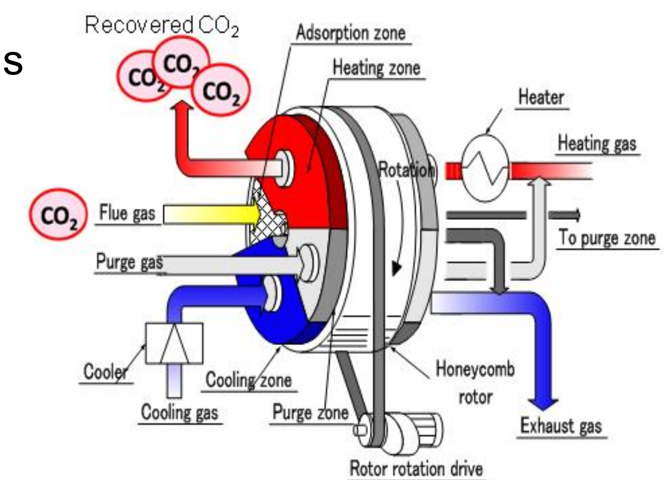
CO_2 Separation and Concentration

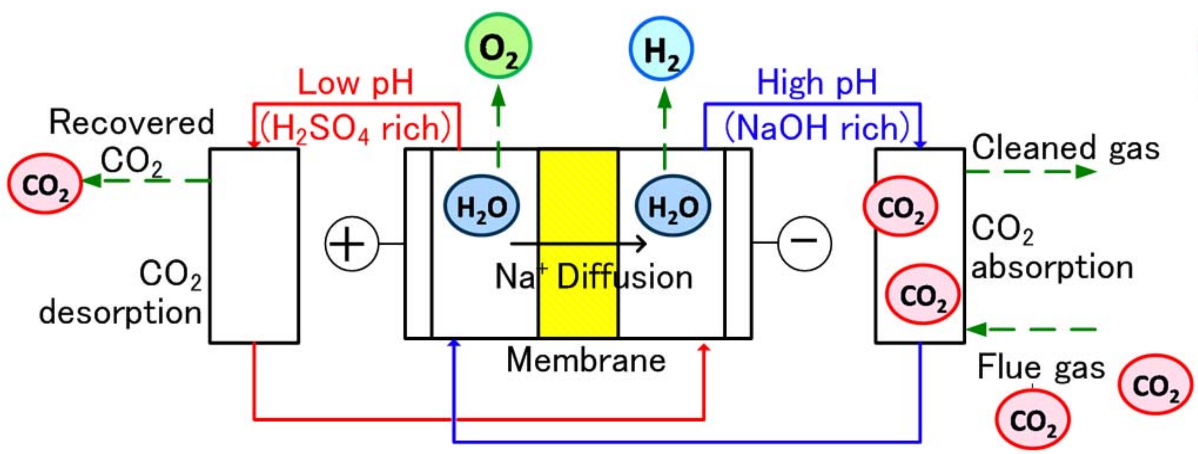
- **Roadblocks**
  - Separation and concentration of CO_2 is energy intensive and expensive
- **Goals**
  - Understand fundamental science underlying mechanisms of absorption and absorption of CO_2 in membranes
  - Establish new high energy efficient CO_2 separation and concentration processes
- **Technical approach**
  - Understand CO_2 separation mechanism for electrochemical and absorption methods at nano or micro scale
  - Use of molecular dynamics to develop optimal materials

M.Minemoto

K.Kusakabe



CO_2 separation and concentration system by adsorption



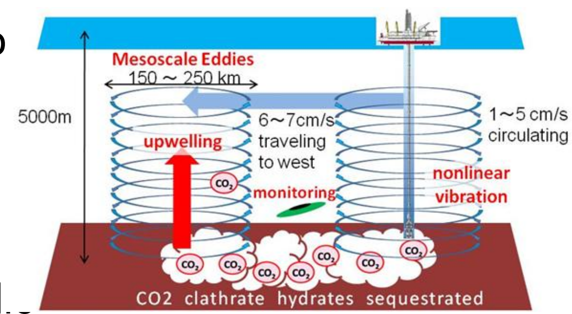
Recirculation liquid: Aqueous solution of Na_2SO_4

CO_2 Capture and Storage

- **Roadblocks**
  - Unknown chemomechanical interactions of CO_2 with fluids, e.g. brine, and porous and fractured rock in relation to the frame of actual deployment
  - Ocean turbulence/ CO_2 transport and interaction from potential leakege of CO_2 from sub-seabed geological formations
  - Impact of increase of CO_2 ocean concentration and decrease of pH on the marine environment and the marine biogeochemical cycling including bathypelagic layers
  - Relationship of actual field data and statistical approaches to reservoir property model inputs
- **Goals**
  - Develop models with predictive capabilities of site integrity over extended periods of time
  - Develop the scientific understanding that will enable the publ. to assess potential benefits and risks of sequestration
- **Technical approach**
  - Geology of Japan and time scales involved will feed back to define basic research requirements
  - Constitutive models for chemistry and fracture of porous rock will be developed to capture the coupling between CO_2 reaction, transport, and mechanics in order to inform models with predictive capabilities of site integrity
  - Develop monitoring system of CO_2 concentration and pH in the deep-ocean/ground


C.T.A.Chen


T.Yanagi



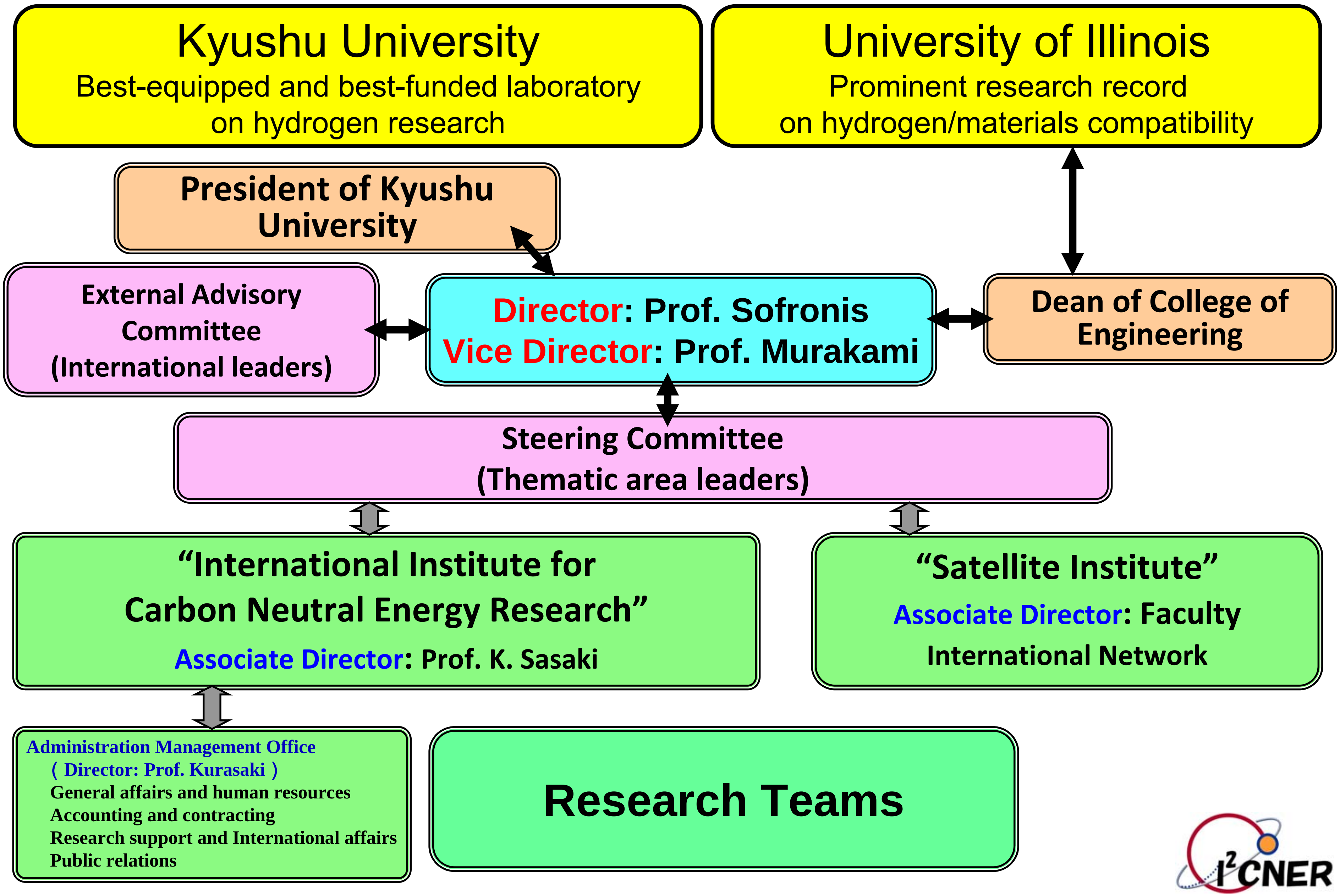
Ocean CCS


Underwater Vehicle for Virtual Mooring

WPI Institutes

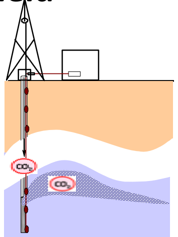
- **International Institute for Carbon-Neutral Energy Research (Kyushu University)**
- **Advanced Institute for Materials Research (Tohuku University)**
- **Institute for the Physics and Mathematics of the Universe (University of Tokyo)**
- **Institute for Integrated Cell-Material Science (Kyoto University)**
- **Immunology Frontier Research Center (Osaka University)**
- **National Institute for Materials Nanoarchitectronics**

I²CNER Administrative Structure



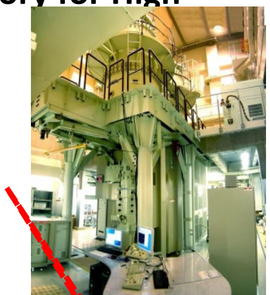
ITO Campus
World Class Academic Environment

CO_2 Natural Analogue Test Field

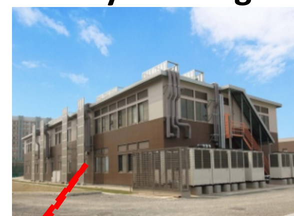


Advanced Project Center

Research Laboratory for High Voltage Electron Microscopy

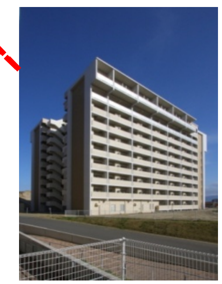


Institute for Materials Chemistry and Engineering



INAMORI Frontier Research Center

Seakeeping and Manoeuvring Basin/ High Speed Circulating Water Channel



Center of Advanced Instrumental Analysis

Hydrogen related Facilities

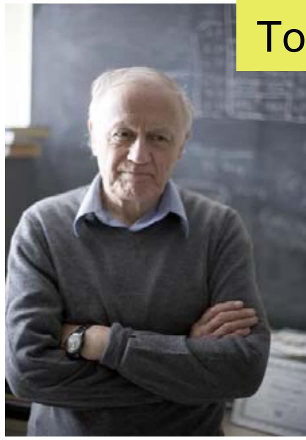
New Facility will be built for WPI

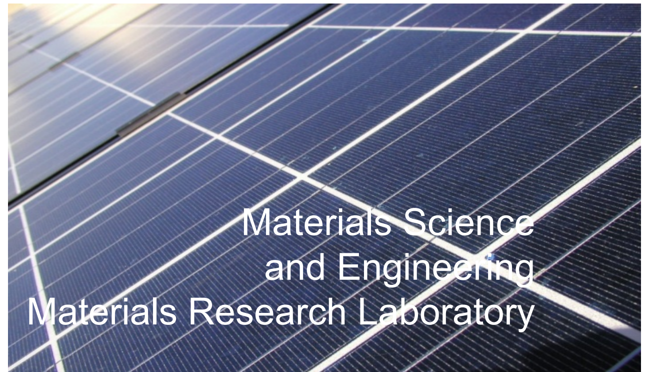
Illinois: A Tradition of Leadership and Impact

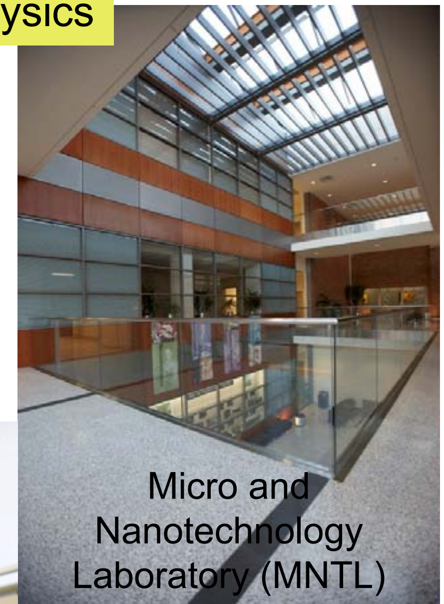
Top-Ten Engineering Graduate Programs

1. MIT
2. Stanford
3. UC Berkeley
4. Georgia Tech
5. Illinois
6. Carnegie Mellon
7. Caltech
8. Michigan
9. UT Austin
10. Cornell

Tony Leggett: 2003 Nobel Prize in Physics

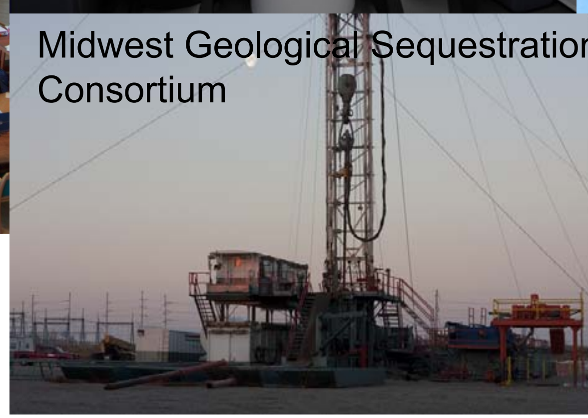






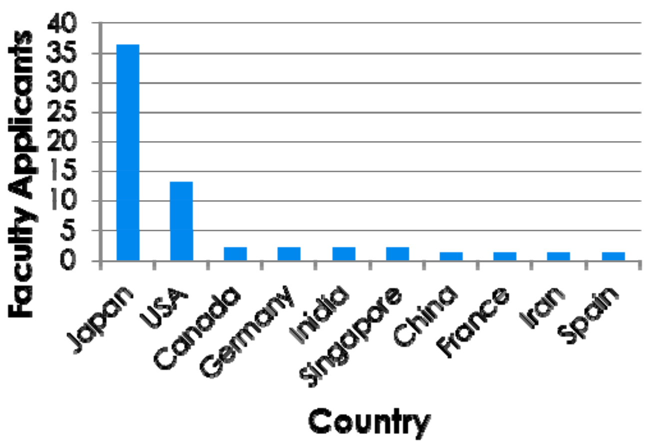
Grainger Engineering Library

Largest engineering library in the nation

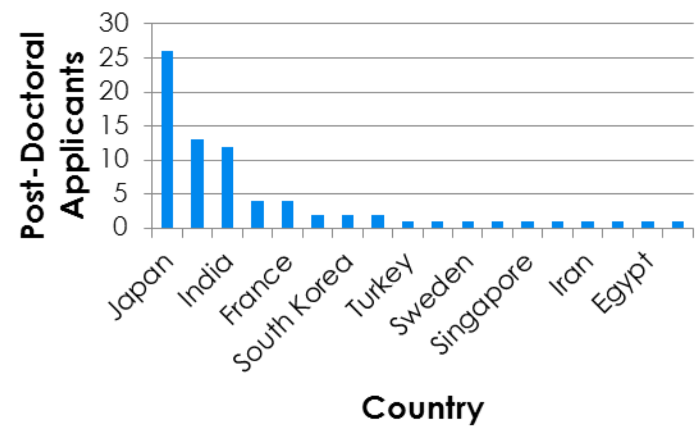


Recruiting New Faculty/Post-docs

- **Faculty Recruiting Committee**
  - Chair
  - Members from Internal Advisory Committee
  - Members with additional expertise
  - Candidate Interviews
    - Seminar presentation
    - Candidates meet with members of the Institute
  - FRC submits recommendation
  - Decision by Director in consultation with Vice-Director and Associate Director



- **Aim at 30% foreign appointments**
  - Advertised
    - Nature, Science, International journal of Hydrogen Energy, The Chemical Society of Japan, The Electrochemical Society of Japan, JOM/TMS(The Minerals, Metals & Materials Society), American Chemical Society, Chemical and Engineering News
  - 61 faculty applicants
  - 75 post-doc applicants



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Why we Believe we can be Successful

- **Partnerships in place**
  - **Midwest Geological Sequestration Consortium (Director Rob Finley)**
  - **UC Berkeley (Ongoing research collaboration with MSE Department)**

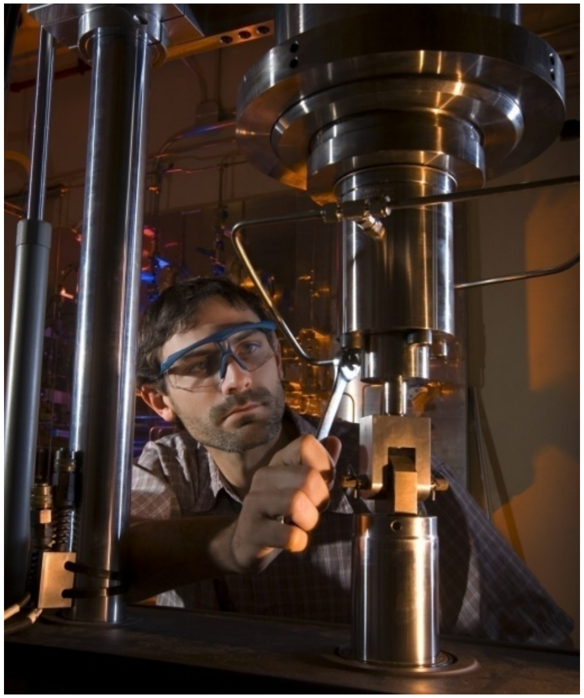
- **Industrial partnerships**
  - **Emerging technologies for hydrogen compression**
    - **Mohawk Innovative Technology Inc. (Dr. Said Jahanmir, Vice President)**
    - **Concepts NREC**
  - **ExxonMobil Research and Engineering Center**

- **Partnerships to be pursued**
  - **Argonne National Laboratory (Energy Storage)**

- **Livermore Valley Open Campus (LVOC) (In progress, NNSA funding)**
  - **Sandia National Laboratories, Livermore (WPI office on site)**
  - **Lawrence Livermore National Laboratory**

Sandia National Laboratories Partnership with I²CNER

Livermore Valley Open Campus



- **Leverage 40+ years in H_2 effects on structural materials at SNL**
  - Facilities for testing materials in high-pressure H_2 unique in North America
- **Existing collaborations demonstrate productive role for SNL**
  - SNL/Illinois collaborations on H_2-structural materials since 2002
- **DOE encouraging collaborations with Japan**
  - Strong DOE support of relationship between new WPI and LVOC-H_2
  - WPI will be able to leverage the LVOC-H2 unique experimental and near-Pacific collaborative facilities

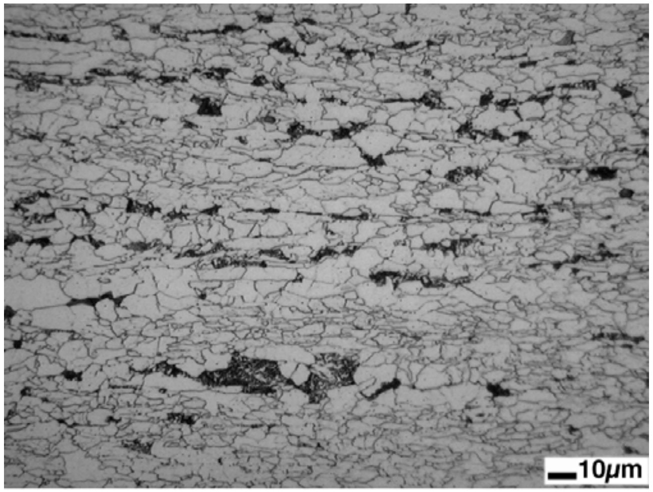
“Fukuoka Team” for hydrogen energy

Current API Transmission Pipeline Alloy Designs
Potentially Embrittlement-Resistant Microstructures

- **Four alloys under evaluation**
  - **Alloy "A" – Demonstrated to be poor in the presence of H_2S sour service natural gas applications.**
  - **Alloy "B" and "C" – Demonstrated to be good, but alloy and microstructure design needs further evaluation.**
  - **Alloy "D" – Excellent. Alloy and microstructure design currently used and specified in H_2S sour service natural gas service.**

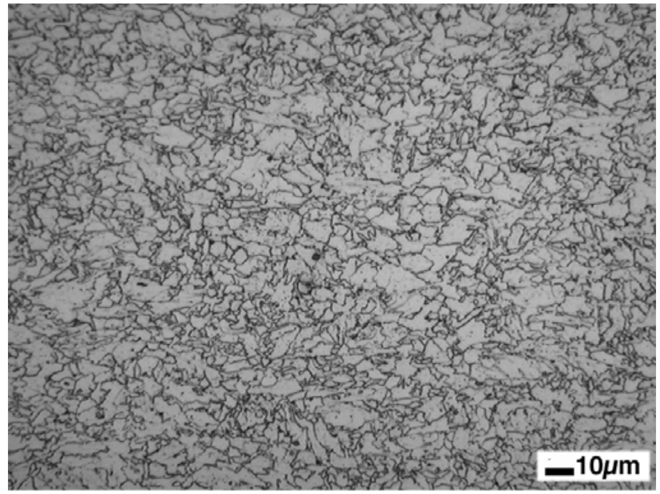
		API/ GRADE	C	Mn	Si	Cu	Ni	V	Nb	Cr	Ti	
Typical natural gas pipeline steel (ferrite/pearlite)	A	X70	0.08	1.53	0.28	0.01	0.00	0.050	0.061	0.01	0.014	poor
Ferrite/acicular ferrite	B	X70/80	0.05	1.52	0.12	0.23	0.14	0.001	0.092	0.25	0.012	better
Very little pearlite mixed with ferrite/acicular ferrite	C	X70/80	0.04	1.61	0.14	0.22	0.12	0.000	0.096	0.42	0.015	good
Ferrite/low level of pearlite	D	X52/60	0.03	1.14	0.18	0.24	0.14	0.001	0.084	0.16	0.014	best

Potentially Embrittlement-Resistant Microstructures

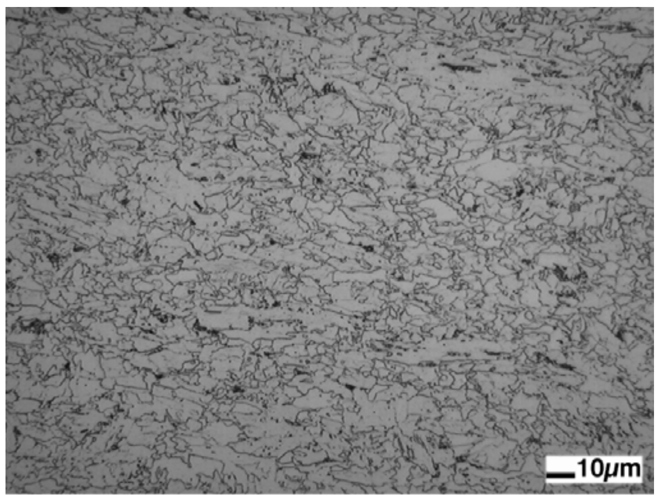


Microstructure of Alloy A shows presence of both ferrite and pearlite

Typical natural gas pipeline steel



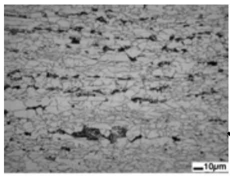
Microstructure of Alloy B shows ferrite and acicular ferrite

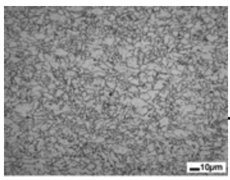


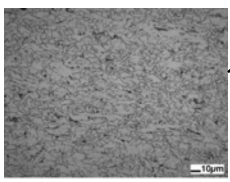
Microstructure of Alloy C shows very little pearlite mixed with ferrite and acicular ferrite

Future Work

- **Experiment**
  - **Construct permeation measurement system and establish the diffusion characteristics of existing and new pipeline steel microstructures**
    - **Existing natural gas pipeline steels provided by AirLequide and Air Products. Specimens are in our laboratory**
    - **New micro-alloyed steels (new microstructures) provided by Oregon steel mills through DGS Metallurgical Solutions, Inc.**







	API/ Grade	C	Mn	Si	Cu	Ni	V	Nb	Cr	Ti	
A	X70	0.08	1.53	0.28	0.01	0.00	0.050	0.061	0.01	0.014	Typical natural gas pipeline steel
B	X70/80	0.05	1.52	0.12	0.23	0.14	0.001	0.092	0.25	0.012	Ferrite/acicular ferrite
C	X70/80	0.04	1.61	0.14	0.22	0.12	0.000	0.096	0.42	0.015	Ferrite/acicular ferrite
D	X52/60	0.03	1.14	0.18	0.24	0.14	0.001	0.084	0.16	0.014	Ferrite/low level of pearlite

    - **Collaboration with Schott North America for coating of our samples**
  - **Determine uniaxial tension macroscopic flow characteristics in the presence of hydrogen**
  - **Carry out fracture toughness testing**
  - **TEM studies on existing and new pipeline material microstructures**
    - **Obtained the first TEM images**
    - **Graduate assistant is learning sample preparation and how to perfect the images**

Description of API Alloy Designs Under Evaluation for Hydrogen Service

- **Alloy design "A" is a typical C-Mn-Si-Dual microalloyed API X70 producing a standard ferrite/pearlite microstructure. This alloy design and microstructure is typical for current pipelines in oil and natural gas service**

- **Alloy designs "B" and "C" are low C, Mn-Si-Single microalloy higher strength capable of producing a ferrite/acicular ferrite microstructure. This alloy design and microstructure is typical for higher strength natural gas pipelines**

- **Alloy design "D" is low C, Mn-Si-Single microalloy lower strength producing a ferrite/low levels of pearlite microstructure. This alloy was purposefully designed for hydrogen induced cracking resistant (HIC) steels used in "sour service" (presence of H_2S) natural gas service**

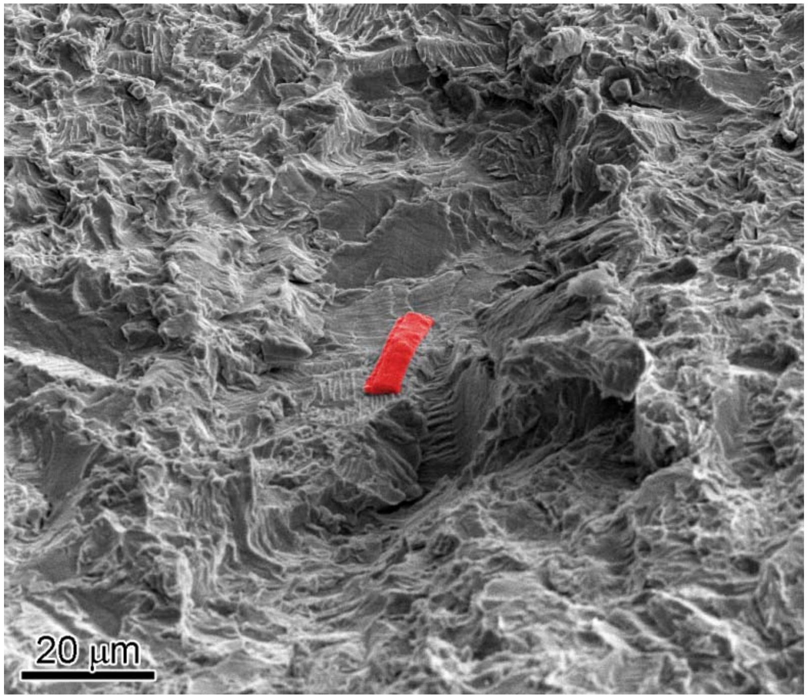
Ranking of Alloy/Microstructure's Under Evaluation Resistance to Hydrogen Embrittlement

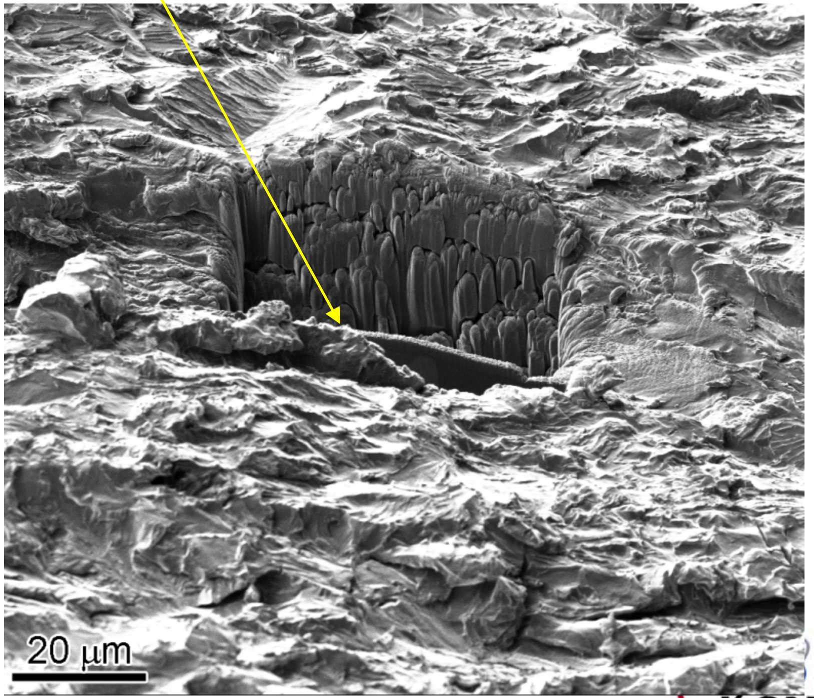
- **Resistance to hydrogen embrittlement and thus suitability for hydrogen service for the four alloy's under evaluation is as follows:**
  - **Alloy "A" – Demonstrated to be poor in the presence of H_2S sour service natural gas applications.**
  - **Alloy "B" and "C" – Demonstrated to be good, but alloy and microstructure design needs further evaluation.**
  - **Alloy "D" – Excellent. Alloy and microstructure design currently used and specified in H_2S sour service natural gas service.**

FIB Difficulties

- Uneven topology
  - Areas of interest may lie in a valley
    - Interfere with line of sight for milling
  - “Flat” may be deceptive
    - Might be angled topology
- Deposition of Pt
  - Vapor flow can be disrupted on rough surface
  - Ion beam could destroy surface

- It takes about 12 hours to extract a sample
- Our success rate is 75%





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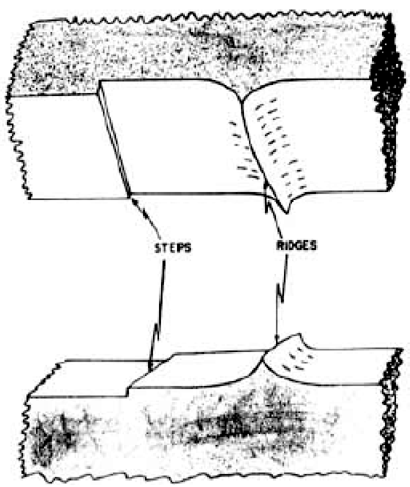
Quasi-cleavage

Definition

- A fracture mode resembling cleavage in that it produces planar or nearly planar fracture facets but differing from cleavage in that the fracture facets are not known to be parallel to cleavage planes

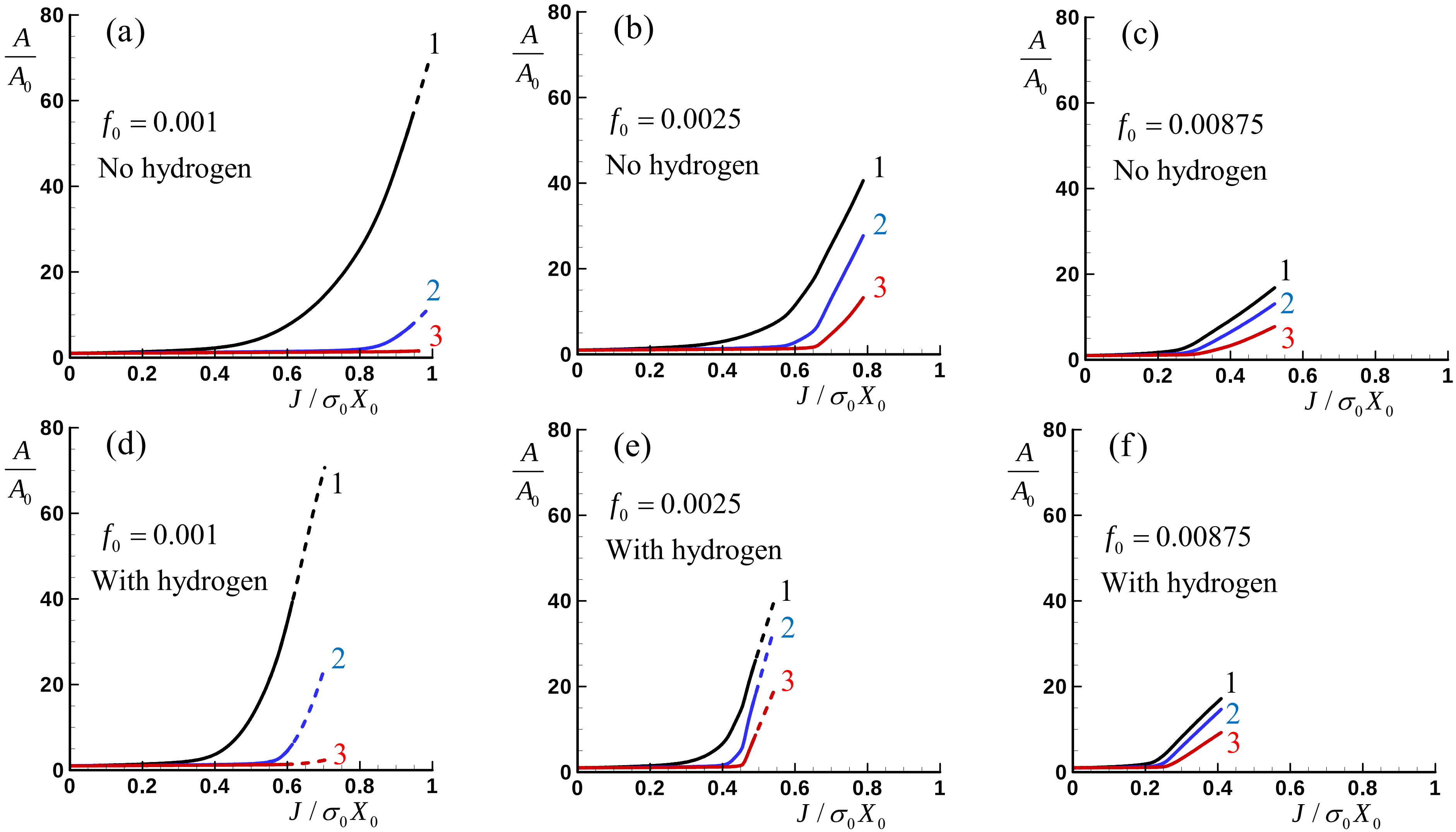
Defining characteristics

- Flat or nearly flat features that do not correspond to a distinct crystallographic plane
- River patterns that are ridges not ledges

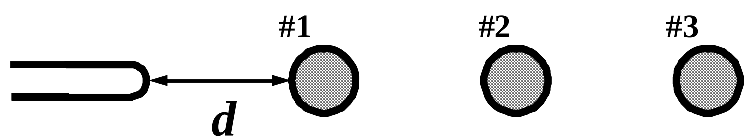


Beachem and Pelloux, 1965

Void Growth at Various Initial Undeformed Volume Fractions



H Increases void growth rate and reduces fracture toughness



Hydrogen Effect on Fracture Toughness of Pipeline Steels

f_0	$J_{IC} / \sigma_0 X_0$		
	No hydrogen	**hydrogen**	**Reduction**
0.0010	0.988	0.703	29%
0.0025	0.790	0.540	32%
0.00875	0.524	0.410	22%

Statistical Model of Hydrogen Induced Fracture

Poisson Postulate: at a given stress σ, the failure probability of an element d*V* equals the area under the frequency distribution of strengths up to that stress, multiplied by the element size

- **Probability of failure** $d\phi$ **ent of volume** dV **under stress** σ

of a single elem

$$d\phi = dV\, f\, N_T^{(c)} \int_0^{\sigma} g(S)\,dS$$

$$N_T^{(c)} \int_0^{\sigma} g(S)\,dS$$

Fraction of particles per unit volume with strength less than σ

- **Weakest link statistics requires that the total survival probability of a volume V is the product of all the elemental survival probabilities**

$$1-\Phi = \prod \left(1-d\phi\right) = \prod \left(1 - dVf\, N_T^{(c)} \int_0^{\sigma} g(S)\,dS\right) = \exp[-f\, N_T^{(c)} \int_0^{V}\int_0^{\sigma} g(S)\,dS\,dV]$$

•Stress distribution around the crack or notch
•Distribution of particle strengths (H concentration)

Failure evaluated at Φ = ½

I²CNER: Looking into Future

- **Contribute toward creating a sustainable and environmentally friendly society by advancing fundamental science to reduce CO2 emissions and establish a non-fossil based energy carrier system**
- **Establish an international network to promote fundamental research for carbon-neutral energy and education**
- **Reform the educational and research culture of Kyushu University to meet the technological challenges of the 21st century**