Hydrogen Embrittlement of Pipeline Steels: Causes and Remediation

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2005 DOE Hydrogen Program Review

May 25, 2005

Project ID #PDP48

Overview

- **Timeline**
  - Project start date: 4/30/05
  - Project end date: 4/30/09
  - Percent complete: 0.1%

- **Budget**
  - Total project funding: 300k/yr
    - DOE share: 75%
    - Contractor share: 25%
  - Funding received in FY04:None
  - Funding for FY05: 300k

Barriers addressed

- Hydrogen embrittlement of pipelines and remediation (mixing with water vapor?)
- Suitable steels, and/or coatings, or other materials to provide safe and reliable hydrogen transport and reduced capital cost
- Assessement of hydrogen compatibility of the existing natural gas pipeline system for transporting hydrogen

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Overview (contd.)

- **DOE Project Coordinator: Mark Paster**
  - Hydrogen distribution program whose goal is to evaluate feasibility of using existing pipeline structure for hydrogen delivery and develop effective practical solutions to address embrittlement issues

- **Industrial Partners: SECAT (Subodh Dass)**
  - Novel coating materials, adhesion issues
    - Applied Thin Films
    - Chemical Composite Coatings
    - Schott North America
  - Current and future pipeline materials
    - Oregon Steel Mills
  - End users/field solutions
    - Columbia Gas Kentucky
    - Napa Pipe Corporation
    - Advanced Technology Corporation
  - Codes and Standards
    - ASME

- **Collaboration with National Laboratories**
  - Oak Ridge National Laboratory
    - Alloy design and development
    - High pressure mechanical property testing
  - Savannah River National Laboratory
    - Weldments
    - High pressure testing

OAK RIDGE NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY

Objectives

- To come up with a mechanistic understanding of hydrogen embrittlement in pipeline steels in order to devise a fracture criterion for safe and reliable pipeline operation under hydrogen pressures of at least 7MPa and loading conditions both static and cyclic (due to in-line compressors)

- To mitigate hydrogen-induced failures by studying the effect on the fracture processes of internal coatings and water vapor/oxygen

- Development of such a fracture criterion and mitigation requires
  - Identification of deformation mechanisms and potential fracture initiation sites in the presence of hydrogen solutes
  - Measurement of hydrogen adsorption, bulk diffusion, and trapping characteristics of the material microstructure in both coatings and pipeline steels
  - Finite element simulation of hydrogen diffusion and interaction with material elastoplasticity under high-pressure hydrogen gas environment

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Approach

- **Solve the coupled problem of material elastoplasticity and hydrogen diffusion at the neighborhood of a crack tip accounting for stress-driven diffusion and trapping of hydrogen at microstructural defects.**
  - Finite element calculations will provide hydrogen concentration profiles ahead of the crack tip as a function of time in terms of the applied load and rate of loading

- **Identify mechanisms and potential fracture initiation sites**
  - Our contention, which needs to be verified through experiment, is that embrittlement is a result of the synergistic action between decohesion at an inclusion/matrix interface (void nucleation) accompanied by shear localization in the ligament between the opening void and the tip of the crack
  - Use experiment, thermodynamics, first principles calculations and the calculated hydrogen amounts to study the cohesive properties of particle/matrix interfaces as affected by the presence of hydrogen solutes

- **Develop a mechanistic model that incorporates the above mechanisms to establish the intrinsic fracture toughness of the material in the presence of hydrogen**
  - See slide #9 for an example case study

- **Carry out experiments and simulations of crack propagation (subcritical crack growth) to determine**
  - The hydrogen effect on the onset of crack growth as described by the extrinsic fracture toughness phrased in terms of the J-integral, J_{IC}
  - The stability of crack propagation to assess catastrophic eventualities

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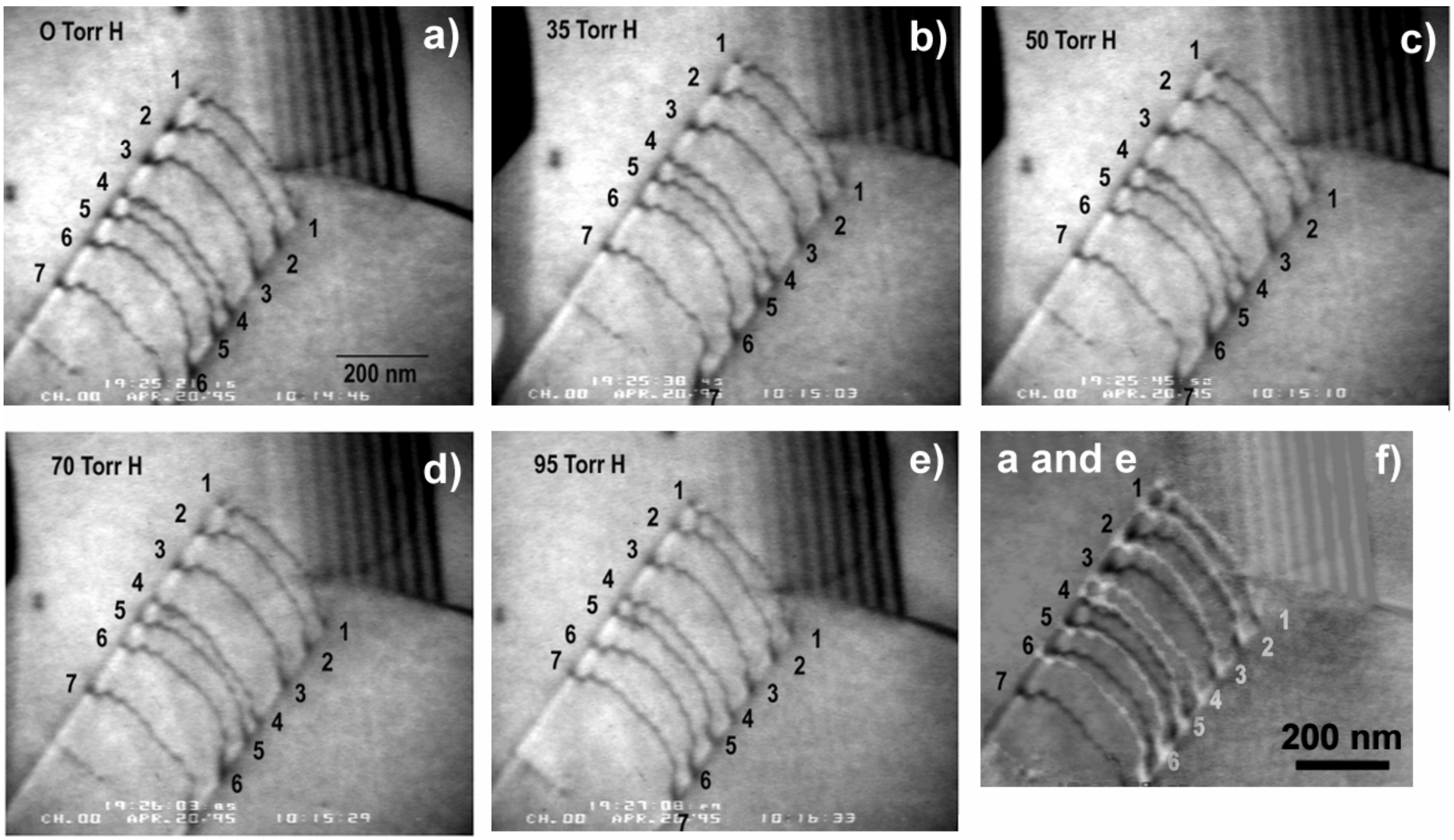
Progress to Date

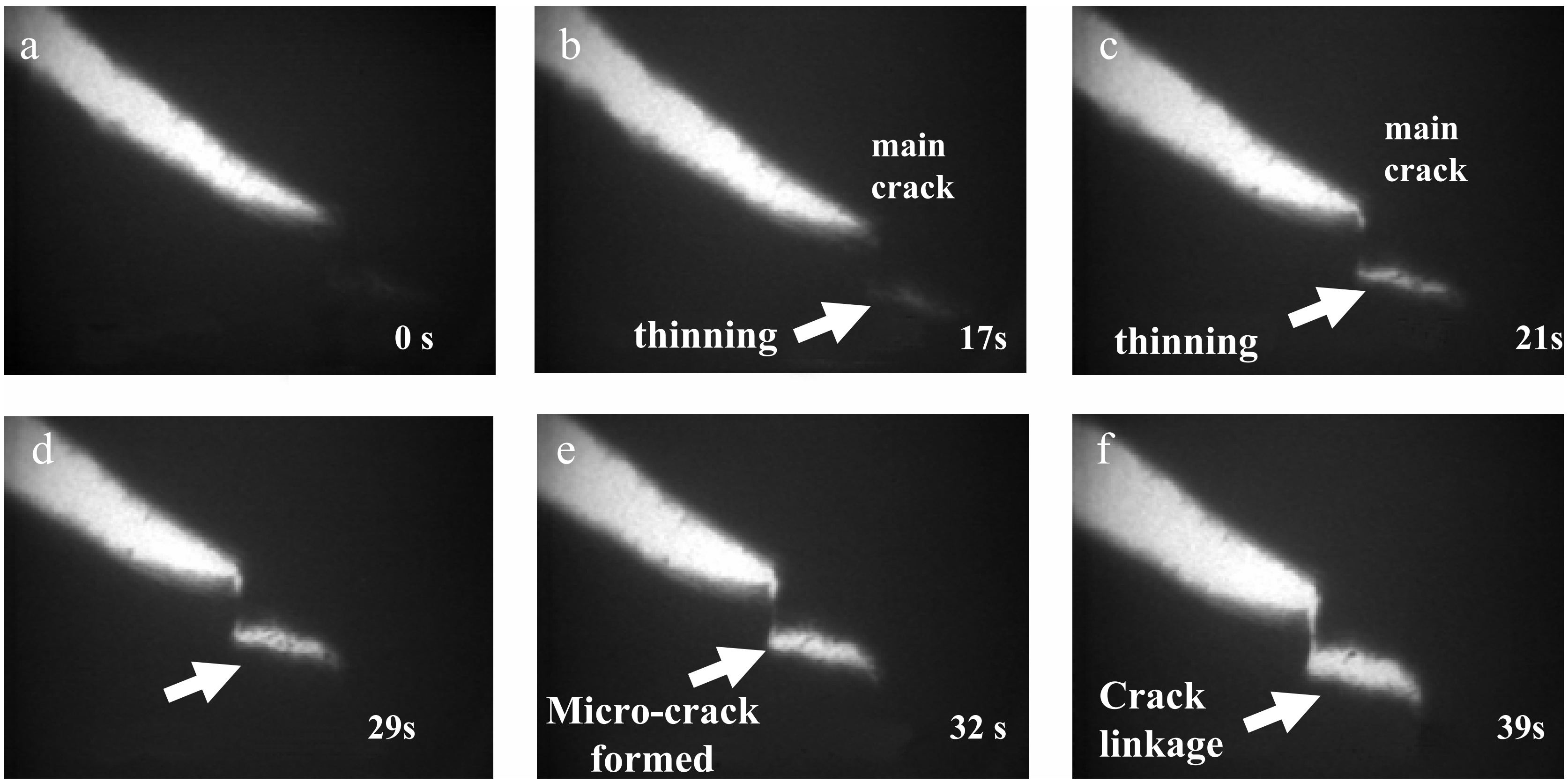
- **Hydrogen enhances the mobility of dislocations and decreases the separation distance between dislocations in a pile-up (e.g. 310S Stainless steel)**



Progress to Date (Contd.)

- Hydrogen enhances crack propagation rates (e.g. IN 903 system)

Static crack in vacuum. Hydrogen gas introduced



Time evolution under constant load

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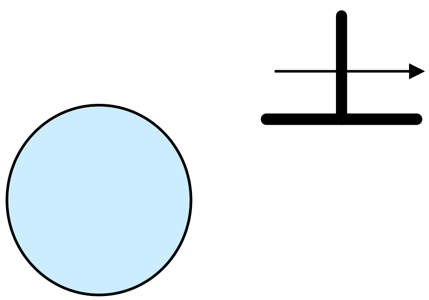
Progress to Date (Contd.)

Hydrogen-Enhanced Plasticity Promotes Hydrogen Embrittlement

Low temperatures or high strain rates

Atmosphere lags behind

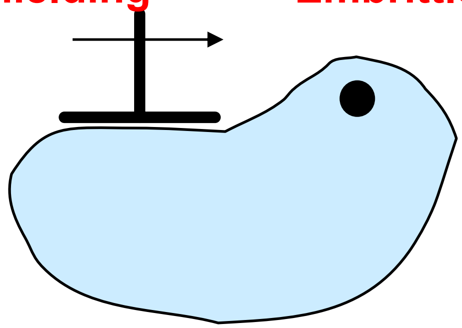


- Both Ni and pure Fe **hardened** by hydrogen at $\dot{\varepsilon} > 10^{-5} s^{-1}$
- Ni is hardened by hydrogen at $T < 200\text{K}$
- Pure Fe is hardened at $T < 100\text{K}$

Intermediate temperatures or low strain rates

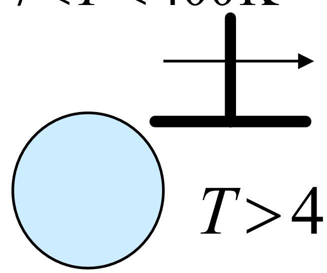
Atmosphere moves with dislocation

- **Shielding** ⟶ **Embrittlement**



Ni $200 < T < 300\text{K}; \quad \dot{\varepsilon} < 10^{-6} s^{-1}$

Fe $77 < T < 400\text{K}$

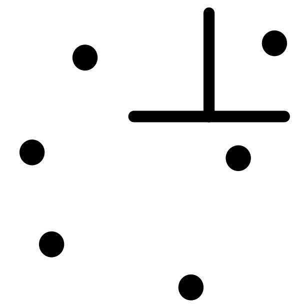


$T > 473\text{K}$

- At higher strain rates atmosphere moves but lags behind ⟶ **hardening**
- Increasing the temperature gives **serrated yielding**

High temperatures

- No atmosphere
- **No hydrogen effect**



$KT > W_B$

$C / C_0 = \exp(W_B / KT)$

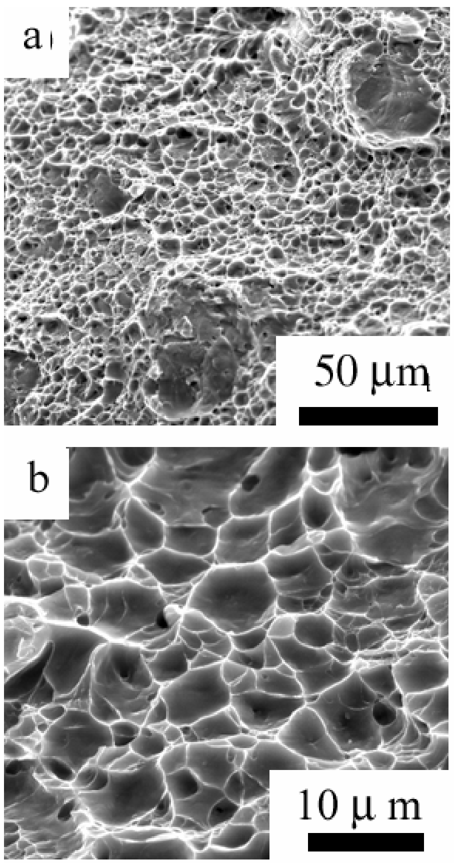
Ni is not embrittled

$T > 473\text{K}$

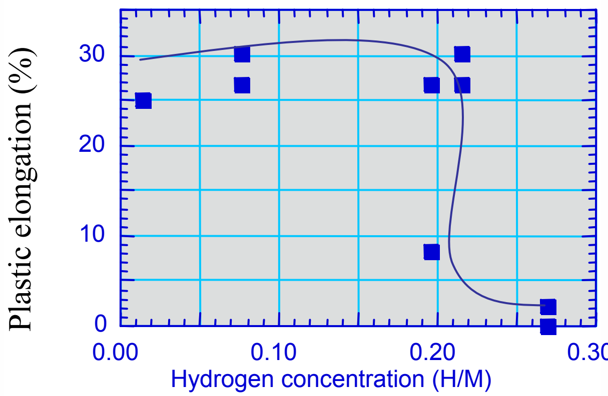
Progress to Date (Contd.)

Hydrogen Promotes Decohesion in BCC titanium

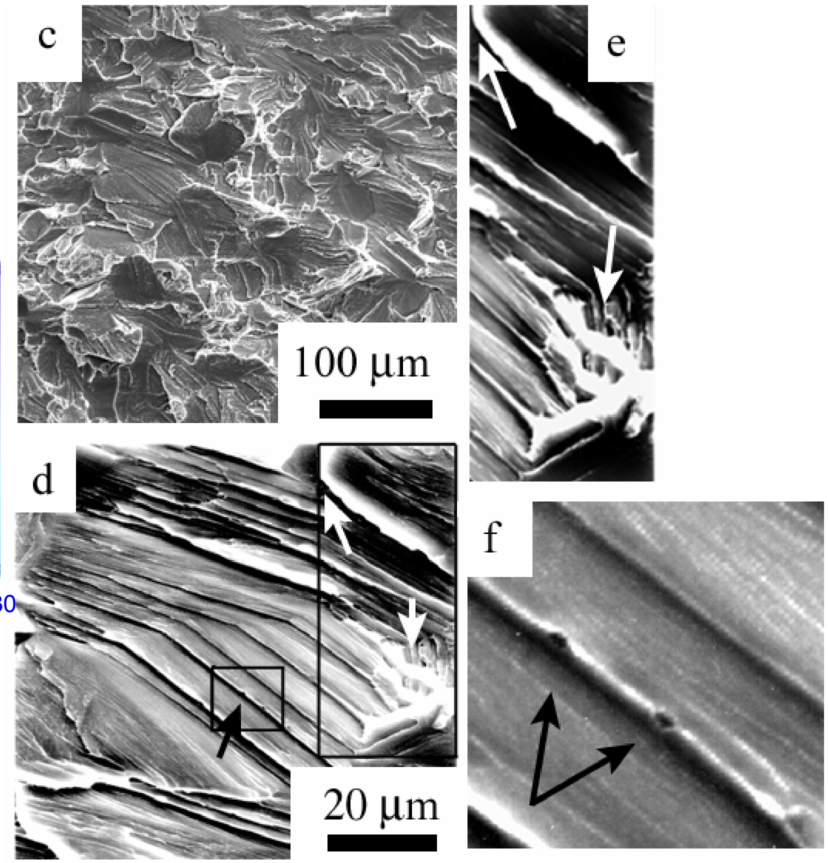
Ductile microvoid coalescence



H concentration <22%



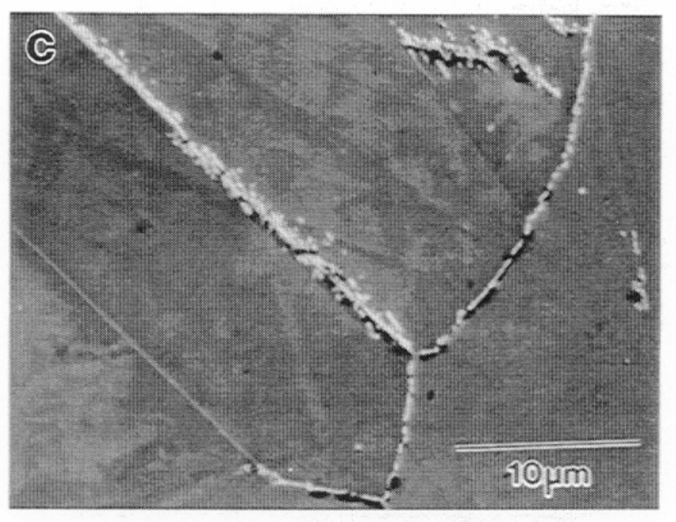
Transgranular cleavage

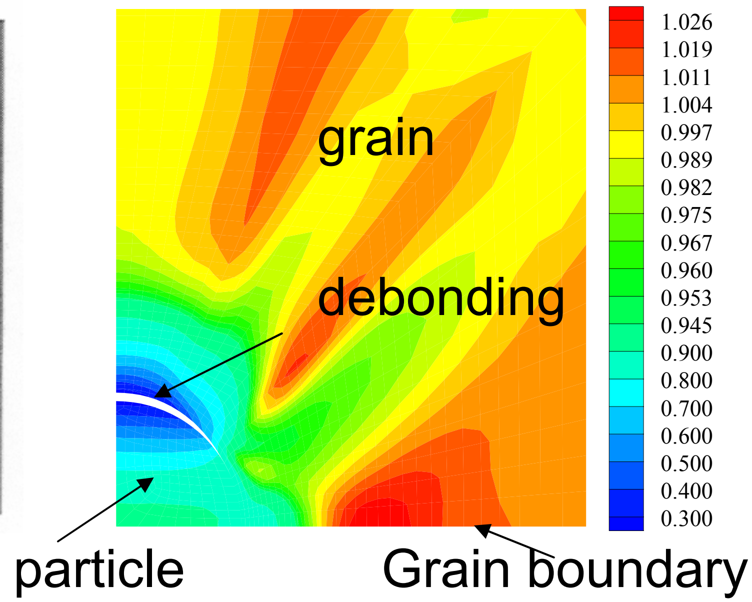


H concentration >22%

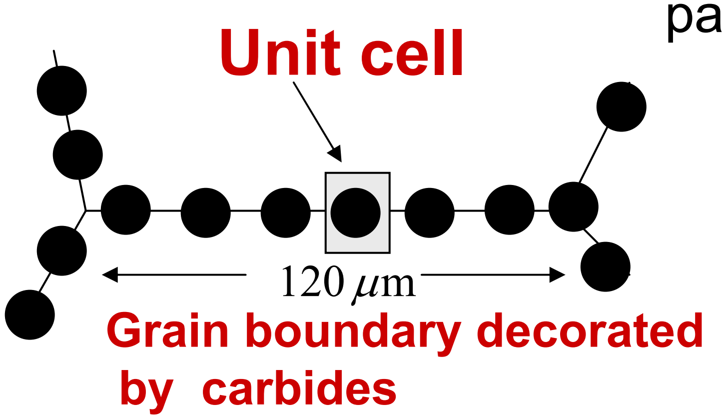
Progress to Date (Contd.)

Finite element modeling of void nucleation at grain boundary carbides in nickel base-alloy 690 and determination of the material intrinsic fracture toughness Γ_H in the presence of hydrogen: $\Gamma_H / \Gamma = 0.53$, where Γ is the fracture toughness in the absence of H.





Contour plots of hydrogen concentration at the first quadrant of the unit cell



- **H assists void nucleation but not growth (H reduces nucleation stress and strain)**
- **H effect on grain boundary cohesion negligible**
- **Failure is controlled by H-assisted void nucleation followed by rapid stress-induced decohesion of grain boundaries.**

Future Work

- **Collaboration with *SECAT, ORNL,* and *Oregon Steel Mills* to identify steel compositions with promising and good hydrogen compatibility**
  - **Carry out mechanical property testing to determine elastic and flow characteristics**
  - **Identify the fracture mechanisms in the presence of hydrogen (accelerated void nucleation and coalescence)**

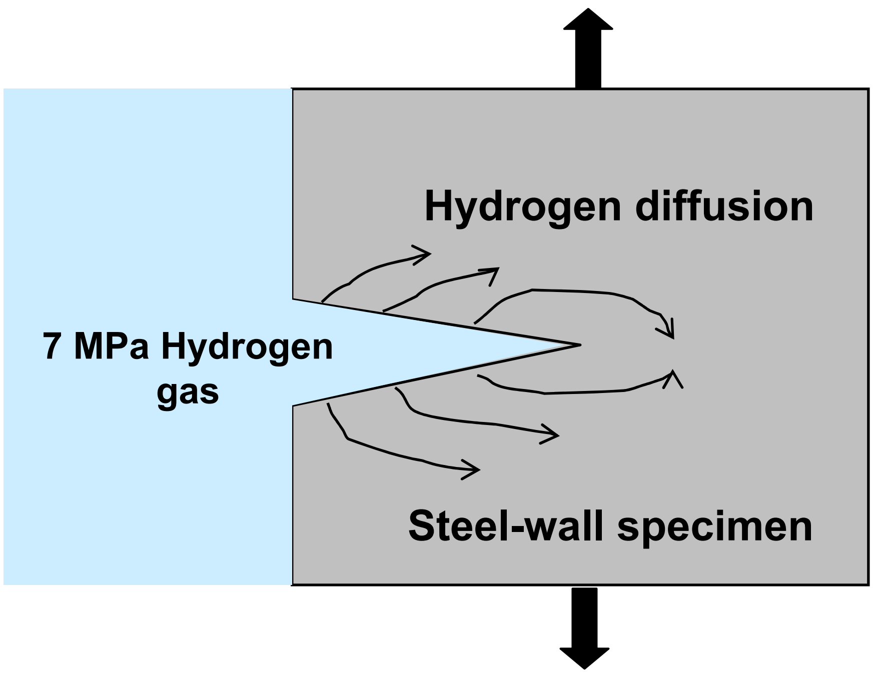
- **Experimental measurement of hydrogen diffusion constant**
  - **One atmosphere measurements at the *University of Illinois***
  - **High pressure measurements at *Oak Ridge National Laboratory and Savannah River National Laboratory***
  - **Identification of the nature of hydrogen traps and measurement of their binding energy through Thermal Desorption Spectroscopy**

- **Begin work in collaboration with SECAT (Applied Thin Films, Chemical Composite Coatings, Schott North America) on how a thin coating film over the steel surface affects hydrogen adsoprtion and subsequent diffusion through the film toward the interior of the steel wall**
  - **Experiments and fist principle calculations on adsorption**

Future Work (contd.)

Finite element simulations of transient hydrogen diffusion coupled with material elastoplastic deformation at a crack tip in a pipeline steel. Account for hydrostatic stress drift and trapping at material defects

$$\frac{D}{D_{eff}}\frac{dC}{dt} = DC_{,ii} - \left(\frac{DV_H C}{3RT}\sigma_{kk,i}\right)_{,i} - \alpha\theta_T \frac{\partial N_T}{\partial \varepsilon^p}\frac{d\varepsilon^p}{dt}$$



d/dt = time differentiation

C = Hydrogen concentration

D = diffusion coefficient

D_{eff} = Effective diffusion accounting for trapping

σ_{kk} = hydrostatic stress

ε^p = plastic strain

T = temperature

V_H = partial molar volume of H

N_T = trap density

θ_T = trap occcupancy

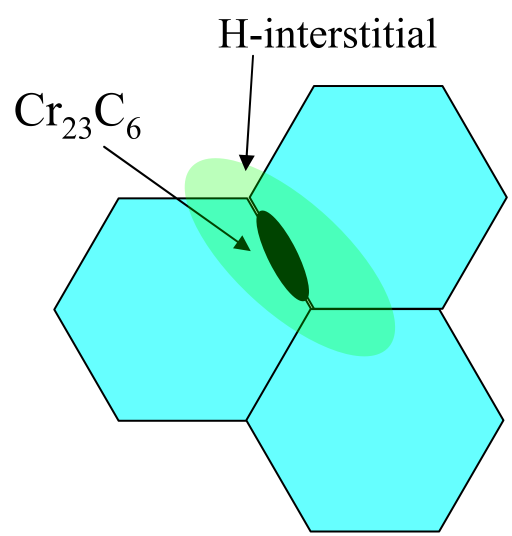
α=trapping sites per trap

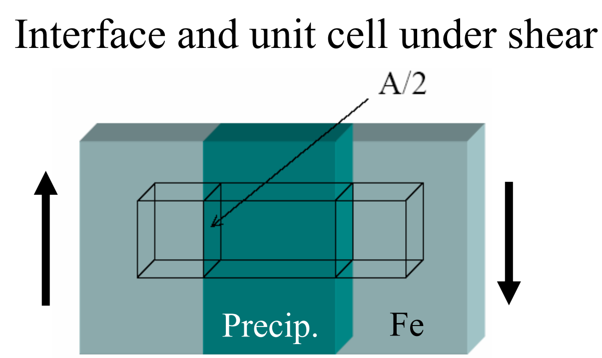
$(\ )_{,i} = \partial(\ )/\partial x_i$

Modify our in-house finite element codes to treat hydrogen diffusion with boundary and initial conditions appropriate to pipeline environment: at time zero crack face concentrations are at equilibrium with hydrogen gas while the bulk/internal hydrogen concentrations are zero

Future Work (contd.)

- **Assessment of interfacial strength of second-phase particles in pipeline steels in hydrogen and water environments**
  - **Ferrite-based alloys have $Cr_{23}C_6$ and MnS precipitates at grain boudnary interfaces. Substitutional solutes (e.g. Cr, Mn, Si) or interstitials (e.g. H, N, C) modify structure and stability**
    - **H (N of C) interstitials alter bonding and cohesion**
    - **Cr is depleted near $Cr_{23}C_6$ interface while Fe preferentially occupies Cr sites not bonded to C**
  - **Obtain cohesive energies via first-principles, Density Functional Theory (DFT) calculations with distribution of atoms near interfaces based on periodic cell approximations**





- **Determine feasibility of using equilibrium criteria to address decohesion at internal interfaces. If not feasible, transient models will be explored via continuum mechanics models (fast-separation limit for interfacial thermodynamics)**

Publications - Presentations

- Robertson, I. M. and Birnbaum, H. K. "Dislocation mobility and hydrogen-A brief review." *Proceedings of the 11th International Conference of Fracture, Symposium on Hydrogen Embrittlement*, (CD-ROM) Torino, Italy, March 20-25, 2005.
- Robertson, I. M. Invited presentation on "The effect of hydrogen in solid solution on the deformation and fracture of metals." Studvik Nuclear Power Company, Studvik, Sweden, 2005.
- Sofronis, P., Aravas, N., Liang, Y., and Dodds, R. J. "Mechanics models for hydrogen-induced shear localization and void growth in materials." *Proceedings of the 11th International Conference of Fracture, Symposium on Hydrogen Embrittlement*, (CD-ROM) Turin, Italy, March 20-25, 2005.
- Somerday, B., Novak, P. and Sofronis, P. "Mechanisms of hydrogen-assisted fracture in austenitic stainless steel welds." *Proceedings of the 11th International Conference of Fracture, Symposium on Hydrogen Embrittlement*, Turin, (CD-ROM) Italy, March 20-25, 2005.
- Bammann, D. J. and Sofronis, P. " A coupled dislocation-hydrogen based model of inelastic deformation." *Proceedings of the 11th International Conference of Fracture, Symposium on Hydrogen Embrittlement*, (CD ROM) Turin, Italy, March 20-25, 2005.
- Sofronis, P. Invited lecture on "Materials for the new hydrogen economy: embrittlement problems and remediation." University of Pennsylvania, Department of Mechanical Engineering and Applied Mechanics, February 2, 2005.
- Sofronis, P. Invited to be the *plenary speaker* on hydrogen embrittlement at the International Symposium of Hydrogen in Matter (ISOHIM 2005) that will take place at the Angstrom Laboratory at Uppsala University, Sweden, June 13-17, 2005.
- Sofronis, P and Robertson, I. M. Invited to give a lecture on "Materials for hydrogen delivery: embrittlement problems and remediation," at the Materials for the Hydrogen Economy Symposium to be held at the Materials Science and Technology 2005 Meeting, Pittsburgh, PA, September 26-28, 2005.
- Sofronis, P. Invited for an extended visit to Japan in 2006 to collaborate with Prof. Murakami at Kyushu University on a joint project of "Fatigue Mechanisms for Steels in Hydrogen Environment "

Hydrogen Safety

- Experimental work on hydrogen-induced material deformation and fracture at 1Atm pressure will be done at the Frederick Seitz Materials Research Laboratory (an interdisciplinary research center funded by the Department of Energy) of the University of Illinois
  - Hydrogen-related safety procedures are already in place according to the University of Illinois regulations on safety. These procedures were followed for hydrogen-related work that was carried out at the Laboratory over the past 20 years.

- Experimental work at pressures >1Atm will be done at the Oak Ridge National Laboratory and Savannah River National Laboratory
  - Both Oak Ridge and Savannah River have hydrogen-related safety procedures in place as high pressure experimental work has already been conducted there.