HYDROGEN EMBRITTLEMENT OF PIPELINE STEELS: CAUSES AND REMEDIATION

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Hydrogen Embrittlement: Long History

M.L. Cailletet (1868) in Comptes Rendus, 68, 847-850

- W. H. Johnson (1875) On some remarkable changes produced in iron and steels by the action of hydrogen acids. *Proc. R. Soc.* 23, 168-175.
- D. E. Hughes (1880) Note on some effects produced by the immersion of steel and iron wires in acidulated water, *Scientific American Supplement*, Vol. X, No 237, pp. 3778-3779.
- Literature is voluminous



Hydrogen Embrittlement: Long History

"On some remarkable Changes produced in Iron and Steel by the Action of Hydrogen and Acids." By WILLIAM H. JOHNSON, B.Sc. Communicated by Prof. Sir WILLIAM THOMSON, LL.D., F.R.S. Received December 7, 1874.

Some three years ago my attention was called to a remarkable change in some of the physical properties of iron caused by its temporary immersion in hydrochloric and sulphuric acids. This change is at once made evident to any one by the extraordinary decrease in toughness and breaking-strain of the iron so treated, and is all the more remarkable as it is not permanent, but only temporary in character, for with lapse of time the metal slowly regains its original toughness and strength. With a view of ascertaining the cause and degree of this change, I have from time to time made a number of experiments, some of which were carried out on a large scale in an iron-works where quantities of sulphuric and hydrochloric acids are used to remove the coating of oxide from iron wire, preparatory to drawing it. Many of these experiments have been already described in a somewhat desultory form in the 'Proceedings of the Literary and Philosophical Society of Manchester' for Jan. 7th, March 4th, Dec. 30th, 1873, Jan. 13th, March 10th and 24th, 1874.

As mentioned before, I first noticed that iron wire became more brittle after a few minutes' immersion (half a minute will sometimes suffice) in strong hydrochloric or dilute sulphuric acid—a piece breaking after being bent once on itself, while before immersion it would bear bending on itself and back again two or three times before breaking. But perhaps the most remarkable phenomenon was, that if, while still hot from the effort of breaking, the fractured part was wetted, it appeared to froth,



Proc. R. Soc. 23, 168-175, 1875

Hydrogen Embrittlement: Long History

enanceo o transport no so por centra nen paeco deberer de"	Break- ing- strain.	Mean error in breaking- strain.	Elongation of length tested.	Mean error in elongation.	Number of experiments for each result given.
The Followine and	06.5	per cent.	per cent.	per cent.	
$\left.\begin{array}{c} \text{Charcoal-iron wire con-}\\ \text{taining H occluded in}\\ \text{H}^2 \text{SO}^4. \end{array}\right\}$	100	± 1.33	1.3	±0·23	6
Charcoal-iron wire, H expelled by heat	106.62	±7·10	4	± 0.33	6
Charcoal-iron wire con- taining H occluded in H Cl	100	± 0.3	1.41	<u>+</u> 0·41	6
Charcoal-iron wire, H expelled by heat}	105 ·3 5	±1·1	4.6	<u>+</u> 0·33	6

The diminution of elongation and breaking-strain caused by occlusion of hydrogen is very marked in these experiments, but is quite equalled by the following experiments on mild steel containing about 0.227 per cent. carbon. The wires were allowed to remain in very dilute hydrochloric acid about 5 hours, then, when tested, heated to about 100° C. for 12 hours, by which means a portion of the occluded H was expelled.

Proc. R. Soc. 23, 168-175, 1875

Hydrogen Embrittlement: Definition

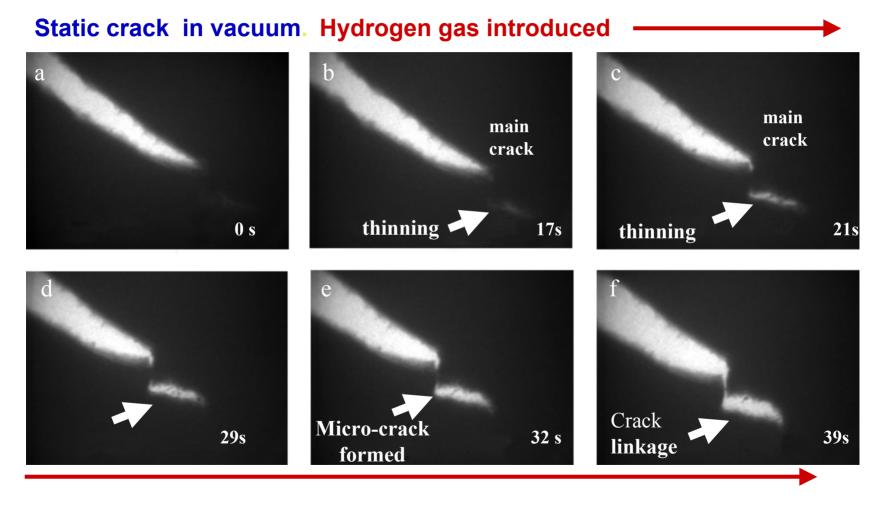
- Material degradation caused by the presence of hydrogen under load. It is manifested in
 - Strain hardening rate
 - Tensile strength
 - Reduction in area
 - Fracture toughness
 - Elongation to failure
 - Crack propagation rate
- Degraded material often fail prematurely and sometimes catastrophically after many years of service

Degradation is influenced by

Microstructure and operating conditions

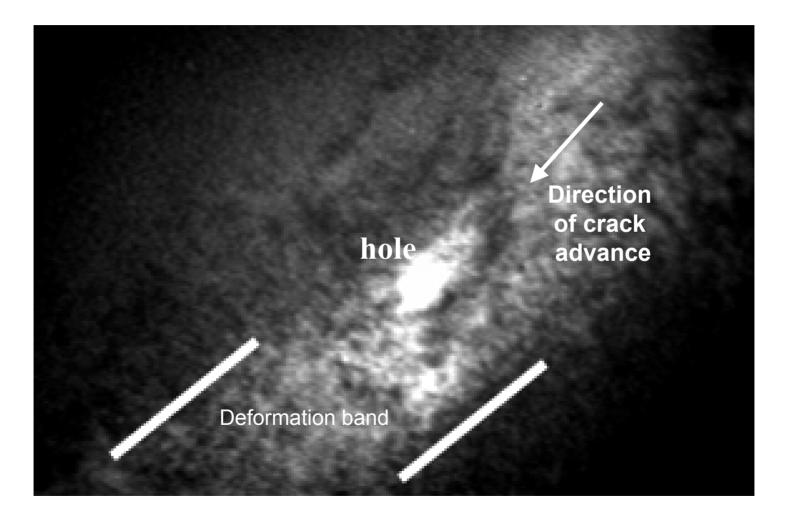


Hydrogen-Induced Crack Propagation in IN903





Crack Propagation in IN 903 Due to Hydrogen





Hydrogen Embrittlement Mechanisms

Several candidate mechanisms have evolved each of which is supported by a set of experimental observations and <u>strong</u> <u>personal views</u>

Viable mechanisms of embrittlement

- Stress induced hydride formation and cleavage
 - Metals with stable hydrides (Group Vb metals, Ti, Mg, Zr and their alloys)
 - Supported by experimental observations
- Hydrogen enhanced localized plasticity (HELP)
 - Increased dislocation mobility, failure by plastic deformation mechanisms
 - Supported by experimental observations
- Hydrogen induced decohesion
 - Direct evidence is lacking
 - Supported by First Principles Calculations (DFT)

Degradation is often due to the synergistic action of mechanisms

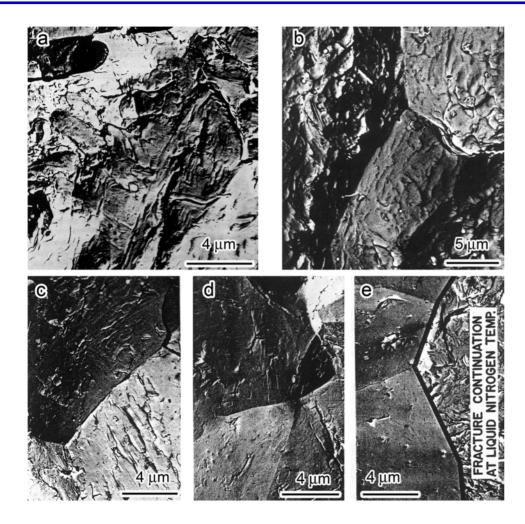


Hydrogen Enhanced Localized Plasticity (HELP)

- Failure is by localized shear processes occurring along slip planes: shear localization
- Transgranular fracture surfaces are highly deformed despite the fact macroscopic ductility is reduced (localized shear processes occurring along slip planes)
- Intergranular fracture occurs by localized ductility in the region adjacent to the grain boundaries
- Applicable to all systems
 - Non-hydride forming systems (Fe, Ni, Al, 304, 310, 316 stainless steel, Ti₃Al, Ni₃Al)
 - Hydride forming systems α -Ti, β -Ti
 - Alloy and high purity systems
 - Bcc,fcc, hcp
- Underlying principle is the hydrogen-induced shielding of the Interactions between microstructural defects



Features on Intergranular Surfaces of a 0.28pct C Steel Fractured in Hydrogen



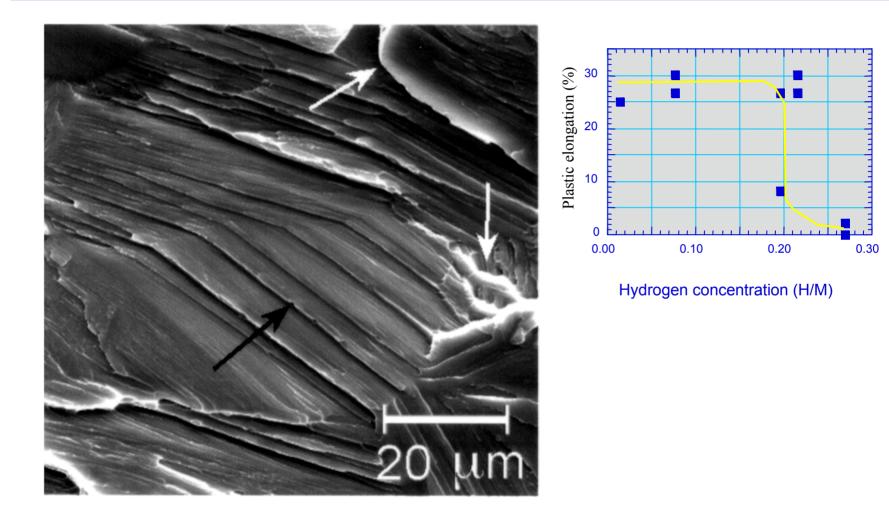
Decrease in the density and size of ductile features (tear ridges) as a function of crack length.

Observations such as these led Beachem to conclude that hydrogen impacts plastic processes.

C. D. Beachem, Met. Trans. 3,437, (1972)



Fracture Surface of a Beta 21S Alloy in Absence of Macroscopic Ductility (Brittle Failure)

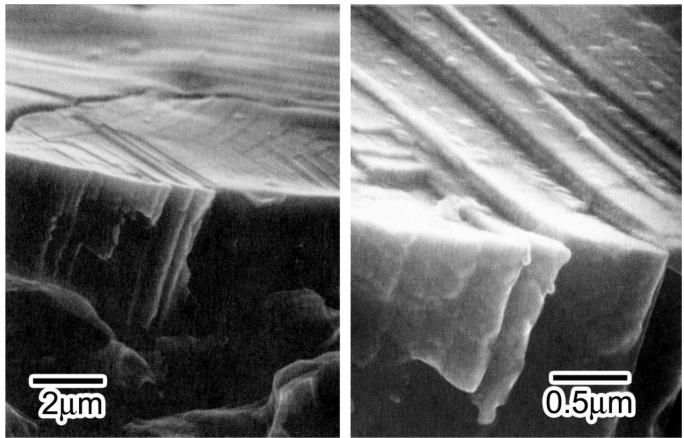




Slip Lines on Brittle Intergranular Facets

310s stainless steel, 5.3 at% H

310s stainless steel, 5.3 at% H

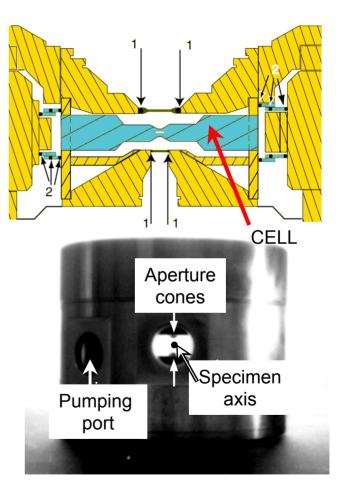


Ulmer and Altstetter, in Hydrogen Effects on Materials Behavior Moody and Thompson, p. 421



Instrumentation: Controlled Environment Transmission Electron Microscope

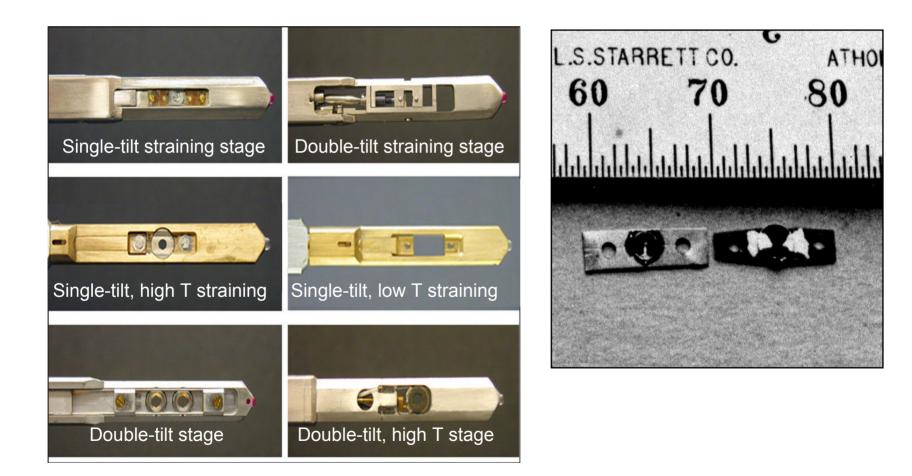




D. K. Dewald, T. C. Lee, J. A. Eades, I. M. Robertson and H. K. Birnbaum Review of Scientific Instruments, 62, 1438, 1991.



Instrumentation: Stages and Samples





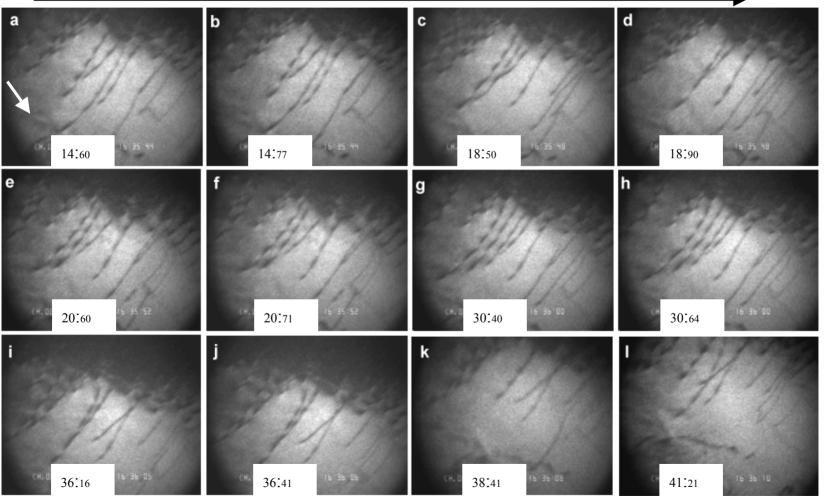
Influence of Hydrogen on Dislocation Mobility (Fe under constant Load and Increasing H Pressure)





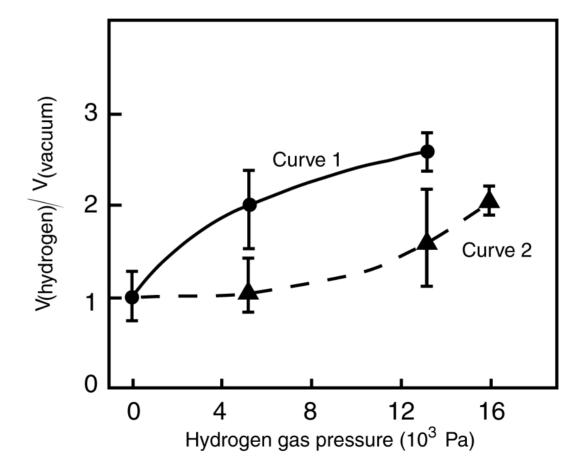
Dislocation Motion in Fe due to Introduction of Hydrogen Gas

Increasing hydrogen gas pressure





Hydrogen Effect on Dislocation Mobility in Ti





Hydrogen-Deformation Interactions

Solute hydrogen atoms interact with an applied stress field

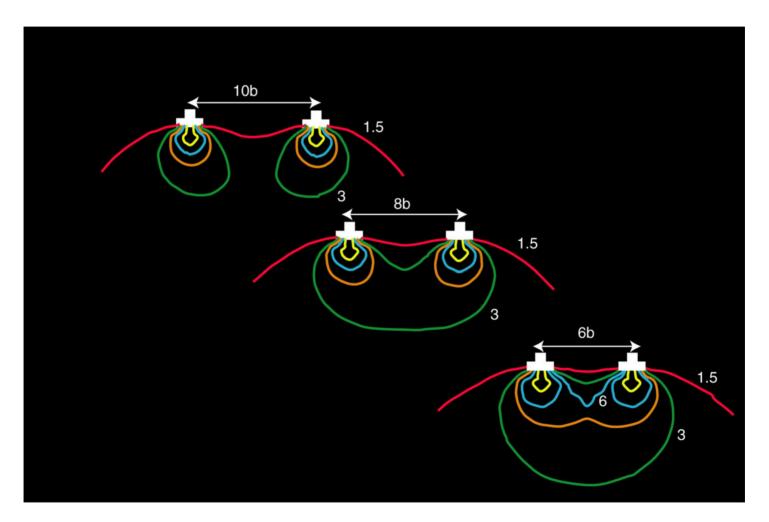
- Hydrogen-induced local volume dilatation (2cm³/mole in Fe)
- Hydrogen-induced local elastic moduli changes (measurements in Nb)

Solute hydrogen diffuses through normal interstitial lattice sites (NILS) toward regions of lower chemical potential, i.e.

- Tensile hydrostatic stress
- Softened elastic moduli

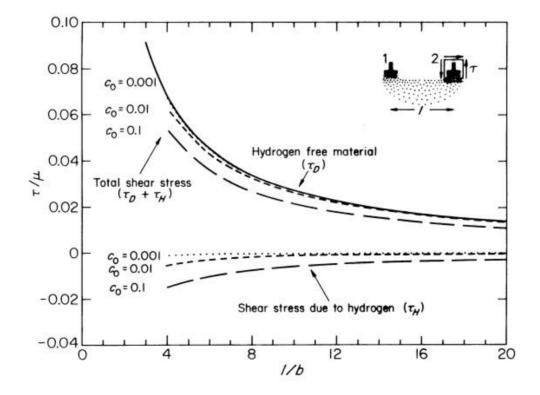


Iso-concentration Contours of Normalized Hydrogen Concentration around two Edge Dislocations in Niobium as the Separation Distance Between the Dislocations Decreases





Effect of Hydrogen Atmospheres around the Two Dislocations: Shear Stress on Dislocation 2 vs Separation along the Slip Plane

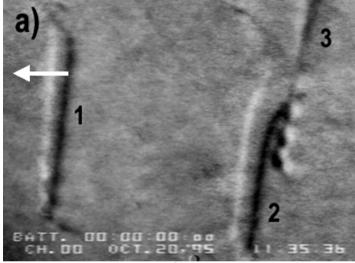


Hydrogen reduces the interaction between dislocations

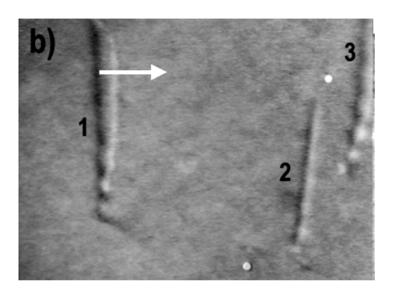


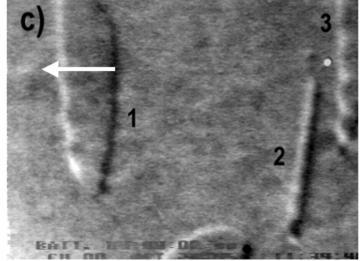
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Reversibility of Hydrogen Effect on Adding and Removing Hydrogen



Pressure increase from 15 to 75 torr





January 2005 Pressure increase from 15 to 75 torr

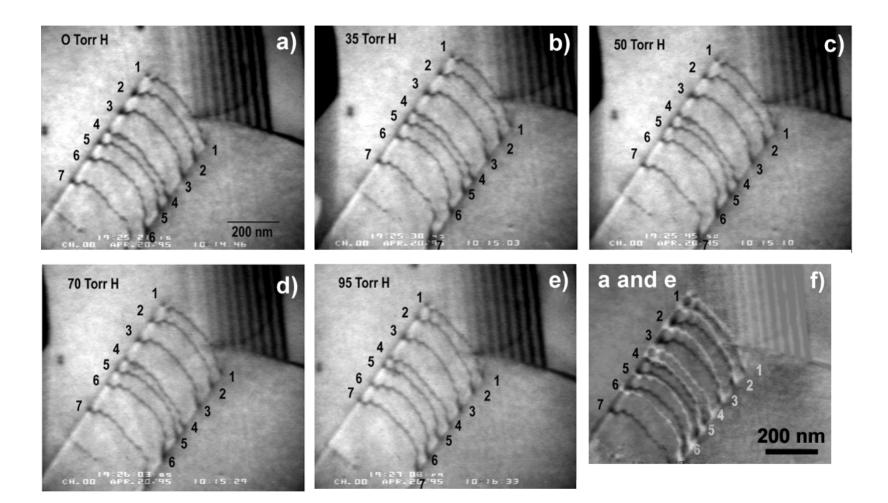
Pressure decrease from 75 to 9 torr

Material: high-purity Al

black - initial position white - final position

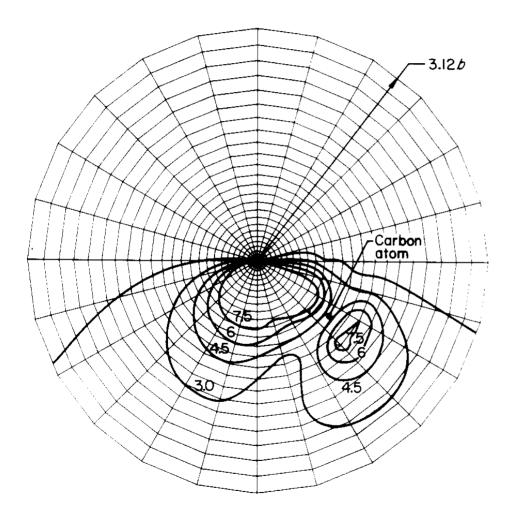


Influence of Hydrogen on Dislocation Separation in a Pile-up (310S Stainless Steel)





Hydrogen-Carbon Interaction

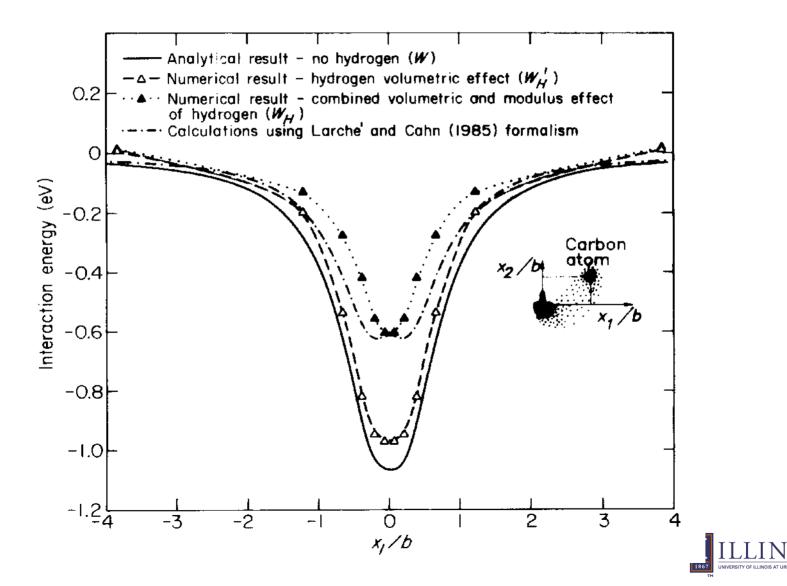


Iso-concentration countours of normalized hydrogen concentration around an edge dislocation and a carbon atom with a tetragonal axis [100]

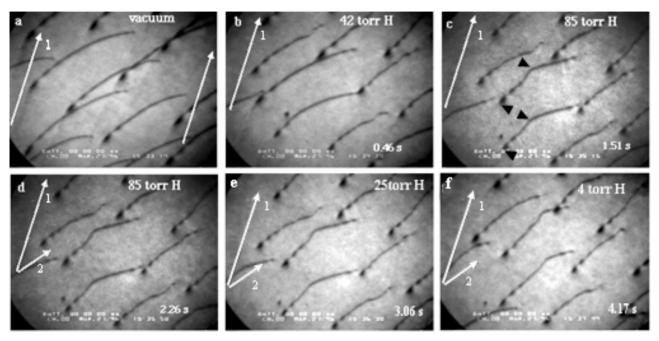
Carbon atom is modeled as a stress center with a tetragonal distortion



Shielding of Interaction Between Edge Dislocation and Carbon Atom



Hydrogen Effect on Dislocation Cross Slip in Aluminum An Alternative Explanation of Increasing Slip Localization



Change in line direction in (c) indicates cross-slip process has initiated.

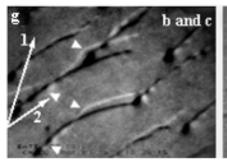
Cross-slip process halted due to hydrogen, (c) and (d).

Cross slip process resumes as hydrogen pressure reduced (f).

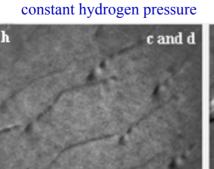


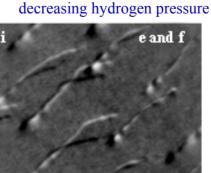
Comparison images

Increasing hydrogen pressure



January 2005-slip in progress.





Cross-slip process halted. Cross slip process resumes

HELP: Conclusions

- Hydrogen enhances the mobility of dislocations and decreases the separation distance between dislocations in a pile-up
- Hydrogen restricts cross-slip by stabilizing edge character dislocations.
- Hydrogen enhances crack propagation rates
- Hydrogen reduces the stacking-fault energy of 310S stainless steel by 20%



HELP and Hydrogen Embrittlement

Low temperatures or high strain rates

Atmosphere lags behind

•Both Ni and pure Fe hardened by hydrogen at

 $\dot{\varepsilon} > 10^{-5} s^{-1}$

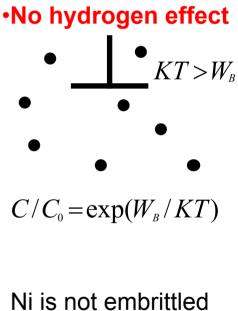
•Ni is hardened by hydrogen at

T < 200K

•Pure Fe is hardened at January 20 $\mathcal{F} < 100 K$

Intermediate temperatures or low strain rates Atmosphere moves with dislocation Shielding —> Embrittlement $200 < \overline{T < 3}00 \text{K}; \dot{\varepsilon} < 10^{-6} \text{s}^{-1}$ Ni Fe 77 < T < 400 K*T*>473K •At higher strain rates atmosphere

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



High temperatures

•No atmposphere

Ni is not embrittled T > 473 K



Critical Issues for the HELP Mechanism

- How does the hydrogen effect on the microscale affect the mechanical behavior on the macroscale?
- How does hydrogen enhance slip localization?
- What are the synergistic effects of other solutes on HELP type fracture, particularly at grain boundaries?
- What is the actual mechanism by which the enhanced plasticity leads to fracture?
 - Localized microvoid coalescence (seen in situ TEM)?
 - Stroh crack due to compressed pile-ups?

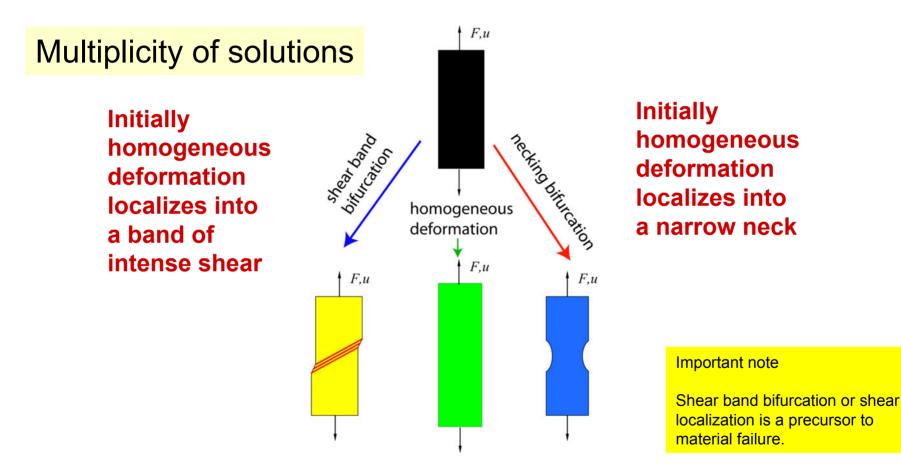


MODELING OF HELP

Connecting the microscopic to the macroscopic



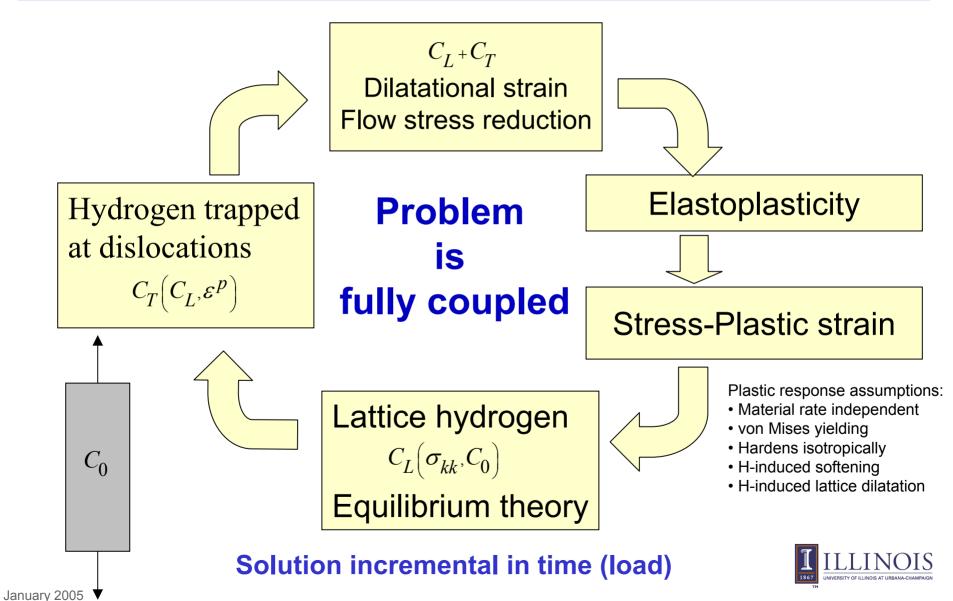
Modeling of Hydrogen-Induced Instabilities in Plane Strain Tension



How does hydrogen affect these instabilities?



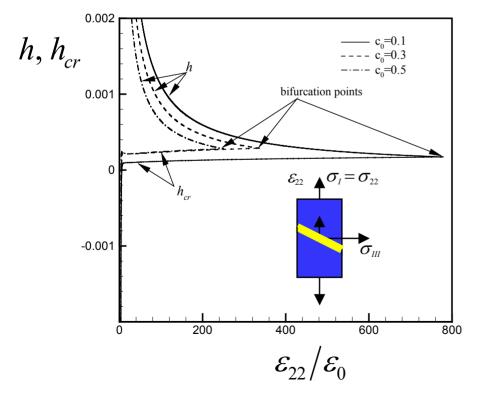
Hydrogen in Equilibrium with Local Stress and Plastic Strain



Condition for Shear Banding Bifurcation

$$h = \frac{1}{3} \left(\frac{\partial \sigma_Y}{\partial \varepsilon^p} + \frac{\partial \sigma_Y}{\partial c} \frac{\partial c}{\partial \varepsilon^p} \right)$$

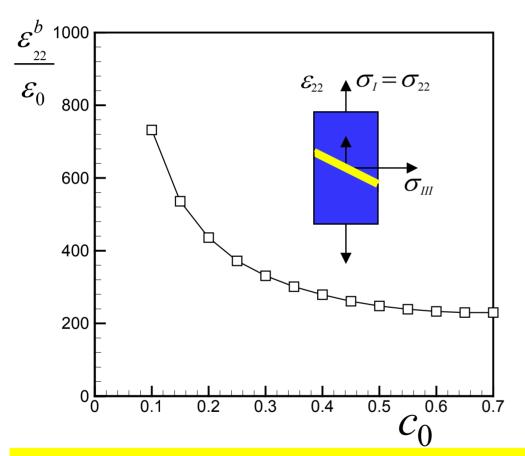
$$\frac{h_{cr}}{G} = \frac{1+\nu}{9(1-\nu)} \left(\beta - \mu\right)^2 - \frac{1+\nu}{2} \left(N_{II} + \frac{\beta + \mu}{3}\right)^2 + \frac{\left(4-3N_{II}^2\right)(1+\nu)}{24\sqrt{3}(1-\nu)} \left(\beta - \mu\right) \left(\sin 2\theta_0\right)^2 \frac{\sigma_e}{G} + O\left(\frac{\sigma_e}{G}\right)^2$$



Dependence of the critical h_{cr} and tangent modulus h on the macroscopic strain for initial hydrogen concentrations of H/M = 0.1, 0.3, 0.5



Critical Strain for Shear Banding Bifurcation in Plane-Strain Tension



Hydrogen triggers shear localization which could never happen in the absence of hydrogen in a work hardening material in plane strain uni-axial tension

Niobium

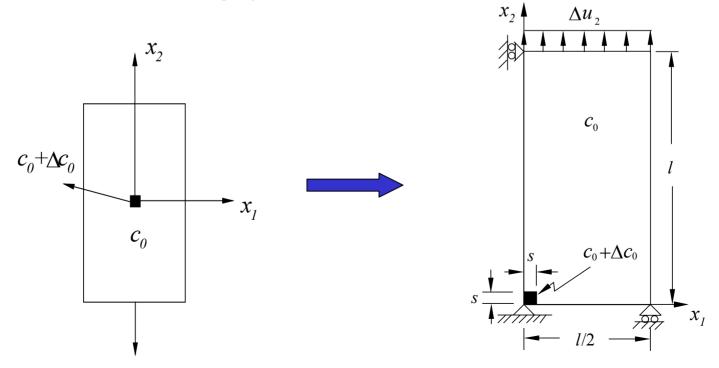
 $\alpha = \beta = 1$ $V_H = 1.88 \text{ cm}^3/\text{mole}$ $\lambda = 0.174$ $V_M = 10.852 \times 10^{-6} \text{ m}^3/\text{mole}$ $N_L = 5.55 \times 10^{28} \text{ Nb atoms/m}^3$ $a = 3.3 \overset{o}{A}$ $W_B = 29.2 \text{ kJ/mole}$ T = 300K $\rho_0 = 10^{10}, \gamma = 2.0 \times 10^{16}$ $\xi = 0.1$ $E = 115GPa, \nu = 0.34$ $\sigma_0 = 400MPa, n = 10$

Present work		Rudnicki and Rice(1975)	
$\frac{1}{3}\left(\frac{\partial \sigma_{Y}}{\partial c^{p}}+\frac{\partial \sigma_{Y}}{\partial c}\frac{\partial c}{\partial c^{p}}\right)$	\rightarrow	h	
$\frac{\Lambda(c)}{\sqrt{3}}\frac{\partial c}{\partial \varepsilon^p}$	\rightarrow	β	
$-\sqrt{3}\frac{\partial \sigma_{Y}}{\partial c}\frac{\partial c}{\partial \sigma_{kk}}$	\rightarrow	μ	
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Hydrogen Perturbation and Plastic Instability

Motivation: Hydrogen concentration at grain boundaries larger than concentration in the bulk of the grain

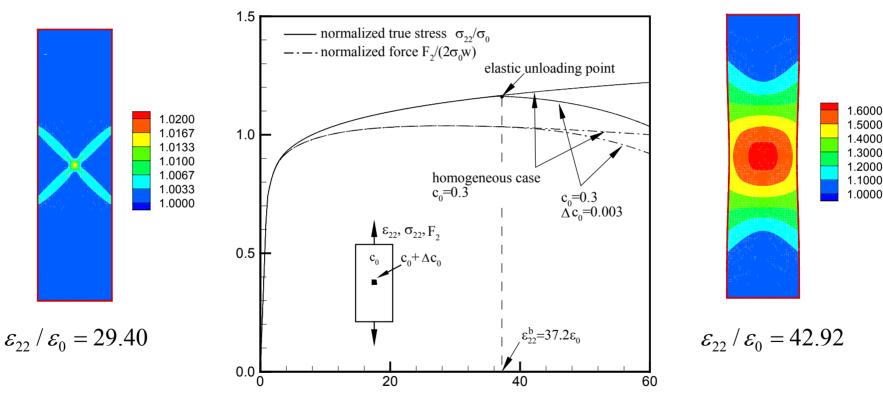
It has been estimated that in nickel at 253K there is a 70nm grain boundary zone in which $C_{zone} = 230C_{bulk}$. In this zone high resolution TEM showed that fracture is a highly localized ductile process



Perturbation in H Concentration to Model Necking Bifurcation in Plane-Strain Tension

$$c_0 = 0.3 H/M \quad \Delta c_0/c_0 = 0.01$$

Local flow stress depends on the local hydrogen concentration

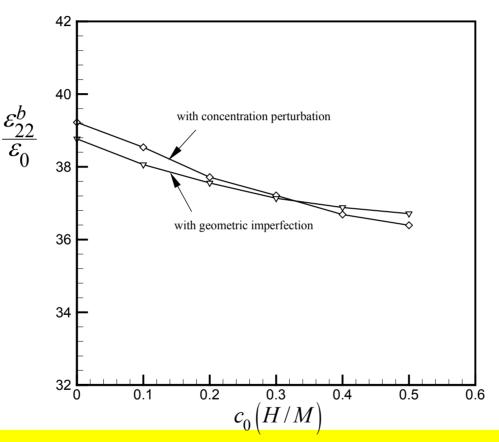


Load attains its maximum at $\varepsilon_{22}/\varepsilon_0 = 28.4$



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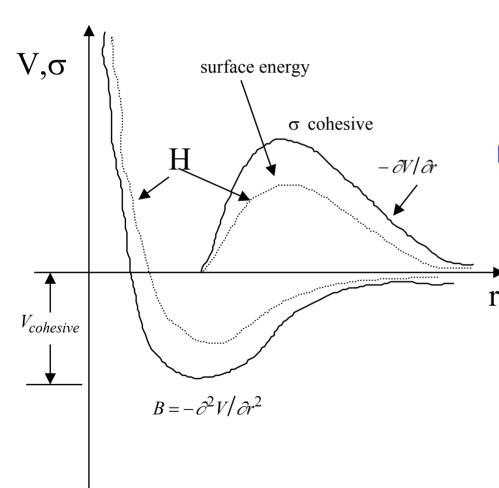
Hydrogen Effect on Necking Bifurcation in Uniaxial Tension



Hydrogen reduces the macroscopic strain at which necking bifurcation commences



Hydrogen-Induced Decohesion



Basic premise: hydrogen reduces the local bond strength which results in the maximum force per unit area required to separate two half solids being reduced.

Problem: magnitude of the reduction is not known, especially under dynamic fracture conditions.



Hydrogen-Induced Decohesion

Experimental evidence

- Cohesive energy: Unaffected by H in NbH fracture energy compared to Nb
- Surface energy: Ni+300ppm H has equal surface free energy to pure Ni
- Cohesive stress (not measured)
- Phonon frequencies and force constant: Increased by H in Vb metals
- Bulk modulus: Increased by H in Vb metals

Ab-initio calculations

- Based on equilibrium fracture considerations hydrogen was found to be a grain boundary embrittler at Ni Sigma 5 (210) GB
- Ideal fracture energy of Fe (110) decreases linearly with H coverage



Hydrogen-Induced Fracture of beta-Titanium as a Function of H Content

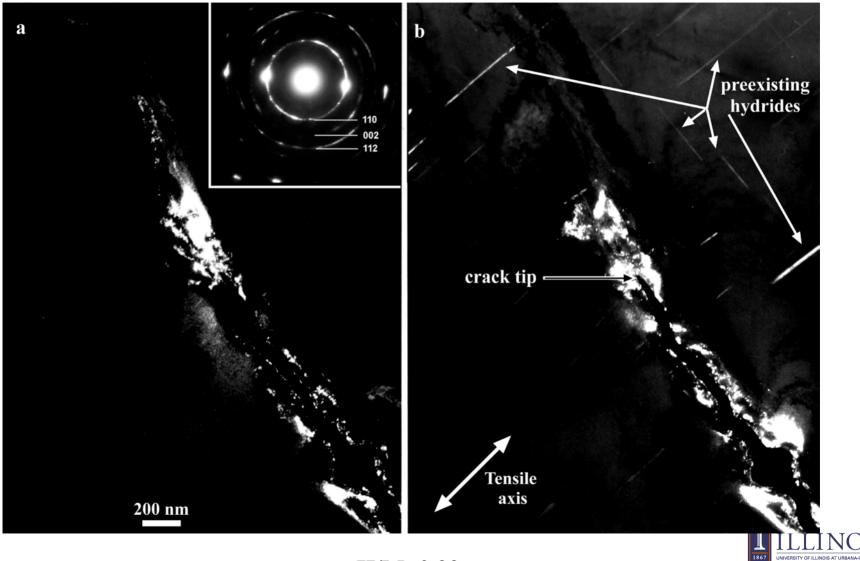
Ductile microvoid Transgranular cleavage coalescence 30 Plastic elongation (% 100 µm 20 50 µm 10 0 0.00 0.10 0.20 Hydrogen concentration (H/M) 20 µm 10 µ m





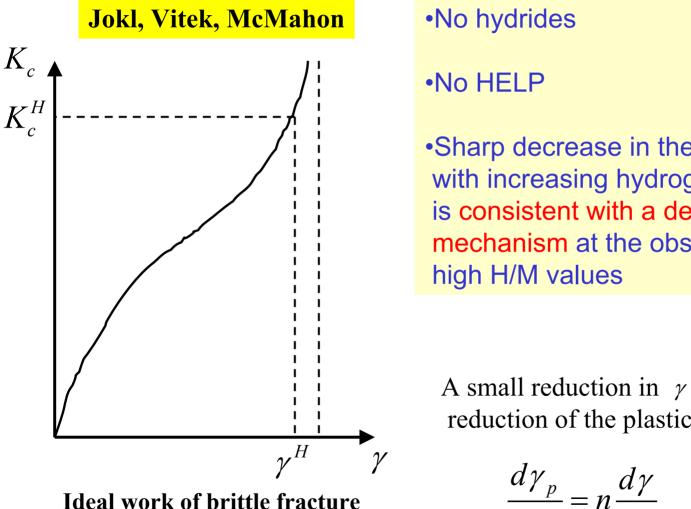
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In situ TEM Deformation of beta-Titanium No New Hydrides at Crack Tip or Along Flanks



H/M=0.29

Hydrogen-Induced Fracture of beta-Titanium



 Sharp decrease in the fracture load with increasing hydrogen concentration is consistent with a decohesion mechanism at the observed

A small reduction in γ brings about a dramatic reduction of the plastic work γ_p for fracture

 $\frac{d\gamma_p}{d\gamma_p} = n\frac{d\gamma_p}{\gamma_p}$ γ_p



Pipeline Steels

Hydrogen Embrittlement under

High-pressure Gaseous Hydrogen Environment



Embrittlement Issues and Phenomenology

- "Mild" steels with yield strength less than 700 MPa and large fracture toughness
 - Hydrogen pressure of at least 14 Mpa for cost equity with natural gas
 - Fatigue due to cyclic loading from in-line compressors
 - There are no studies of embrittlement under these conditions
- Safety design does not allow hoop stress to exceed 80% of yield stress (plastic collapse approach)
 - Cracks propagate before plastic collapse
 - Need for an approach based on Elastoplastic Fracture Mechanics

Residual stresses at girth and longitudinal welds

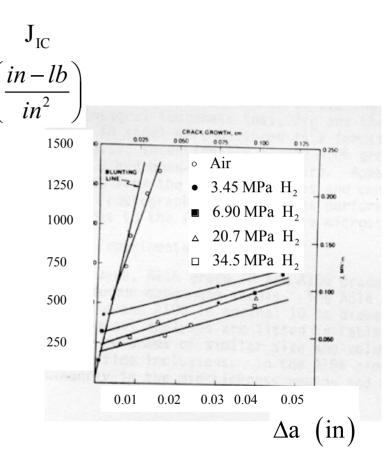
- A weld cannot be efficiently protected by coatings
- Little is known on the interaction between hydrogen solutes and elastoplasticity in the heat affected zone. Especially in the presence of "hard spots" of martensite upon cooling

Stronger steels X-80 and X-100 recently suggested to reduce thickness and diameter are more susceptible to embrittlement



Embrittlement Issues and Phenomenology

- No difference in fracture response between burst and J_{IC} testing (Robinson and Stoltz at A516-70 and A106-B)
 - Less cumbersome and less expensive J_{IC} testing
 - Hydrogen reduces J_{IC} for crack initiation
 - Critical flaw size may be reduced from cm in natural gas to mm in high pressure hydrogen
 - Dramatic tenfold loss of crack growth resistance dJ_{IC}/da
 - Slope dJ_{IC}/da was found independent of hydrogen pressure
 - Hence supply of hydrogen is fast and not the rate limiting process
 - It is the plastic work that controls hydrogen degradation
 - Crack growth resistance dJ_{IC}/da impacts the stability of crack advance
 - Fracture behavior needs to be investigated



Robinson and Stoltz Hydrogen Effects in Metals, 1981, pp-987-995



Fractographic evidence suggests

- Hydrogen-assisted transgranular fracture by void or microcrack initiation through <u>decohesion</u> at second phase particles (precipitate/inclusion) ahead of a crack or notch accompanied by <u>shear localization</u> (HELP) leading to the linking of the void/microcrack with the tip of crack
- Intergranular cracking in welds by hydrogen-induced lowering of grain boundary or matrix/carbide interfacial cohesion in the HAZ
- Our contention, which needs to be verified through experiment, is that embrittlement is a result of the synergistic action of the HELP and decohesion mechanisms



Identify mechanisms of failure

- Transgranular vs intergranular
- Role of inclusions and precipitates
- Fatigue or static loading conditions

Explore for optimum microstructure

- Tempered bainite or tempered martensite superior to pearlitic or pearlite-ferrite steels with speroidized in between
- C: increasing H content gives higher strength but higher H susceptibility
- Mn : ferrite strengthener but reduces fracture toughness in H
- Si: potent ferrite strengthener, neutral to H, problems with formability and weldability
- Ti and Ni: alloying additions may help
- Morphology and volume fraction of inclusions is controlled by S levels
- Silicon steel rather than manganese with fine spheroidized carbides may be a promising system to explore



- Model the failure processes
- Provide an insight to the critical flaw size and its stability
- Device a fracture criterion with predictive capabilities for the incubation period in subcritical crack growth and remnat life of the pipeline
- Study the viability of using high strength steels
 - H incompatibility increases with strength



Mitigate hydrogen embrittlement by adding water vapor in the transported hydrogen

- Water vapor is cheap
- Water vapor is separated easily at final destination stations through cooling
- Water vapor lowers crack growth rates (Robinson, Wei)
 - > Reaction Fe+O \rightarrow FeO is 10⁸ faster than Fe+H₂O \rightarrow FeO+H₂
 - O (inhibitor of crack growth) and H (promoter of crack growth) compete for adsorption sites on the metal surface
- At high transport pressures it is expected that the surface reactions will not be the controlling step. Embrittlement depends on the transport of hydrogen
- Effects of water vapor or O need to be carefully explored in particular at high pressures



Understand the hydrogen or water vapor effects on interfacial cohesion by

- studying the fracture of a thin film attached to a substrate or
- through using "hour-glass radiused" uniaxial tension specimens

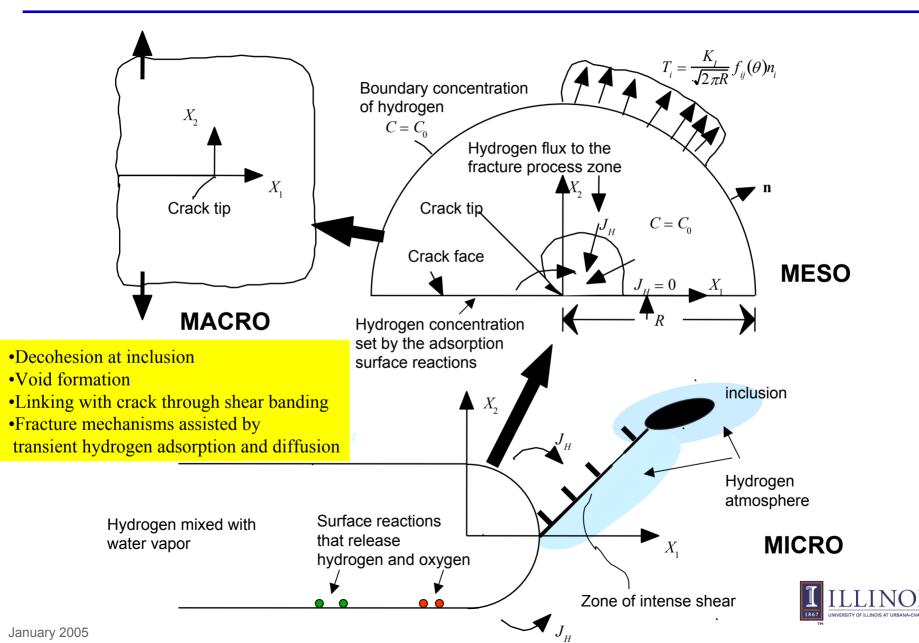


OUTLINE OF AN EXAMPLE STUDY

Transgranular Cracking Initiation - Propagation



Modeling of Ductile Transgranular Fracture: Initiation



Modeling of Ductile Transgranular Fracture: Initiation

Address the role of significant parameters, such as

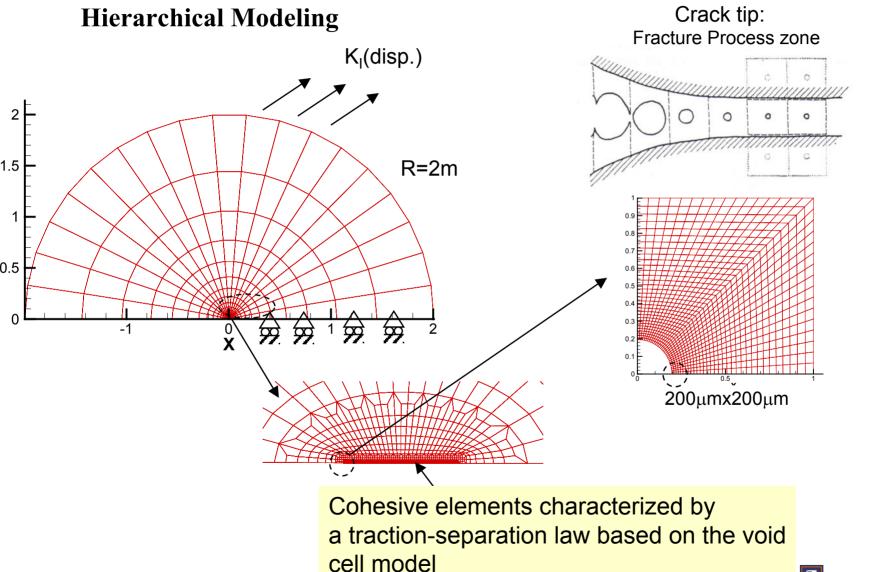
- Material flow characteristics
- Material trapping characteristics (type of traps, trap density, and binding energy)
- Hydrostatic stress
- Plastic strain
- Hydrogen concentration
- Loading rate
- Loading in terms of the applied J-integral
- Adsorption kinetics (ab-initio modeling)
- Cohesive properties of the inclusion/matrix interface (ab initio)
- Lattice cohesion in a direction perpendicular to the slip band (ab-initio)
- Effect of water vapor or other crack growth inhibitors

Hydrogen boundary conditions on the crack face are set by the local adsorption kinetics

• Assumption of first order kinetics leads to hydrogen coverage

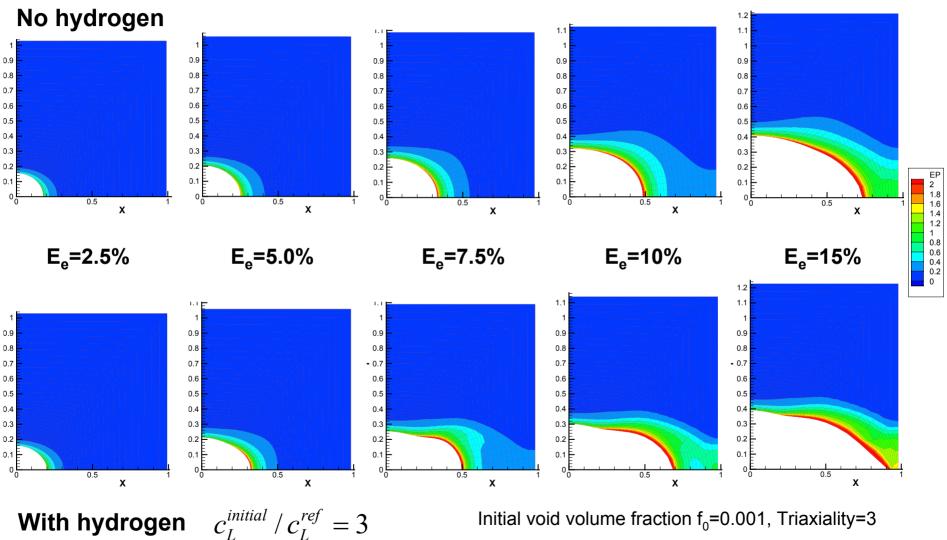
$$\Gamma_h / (\Gamma_h + \Gamma_o) = \left[1 + (k_o p_o / k_h p_h) \right]^{-1}$$







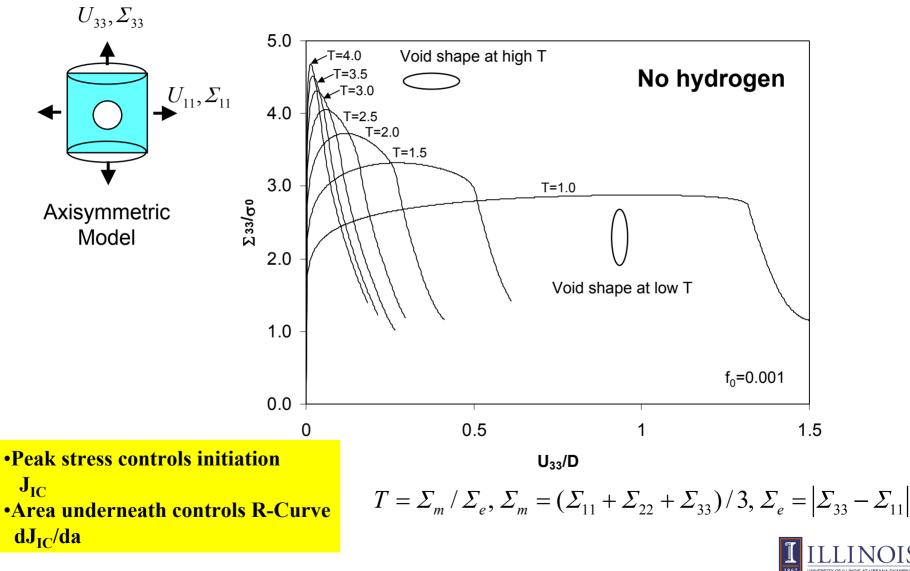
Material Data for A533B Pressure Vessel Steel



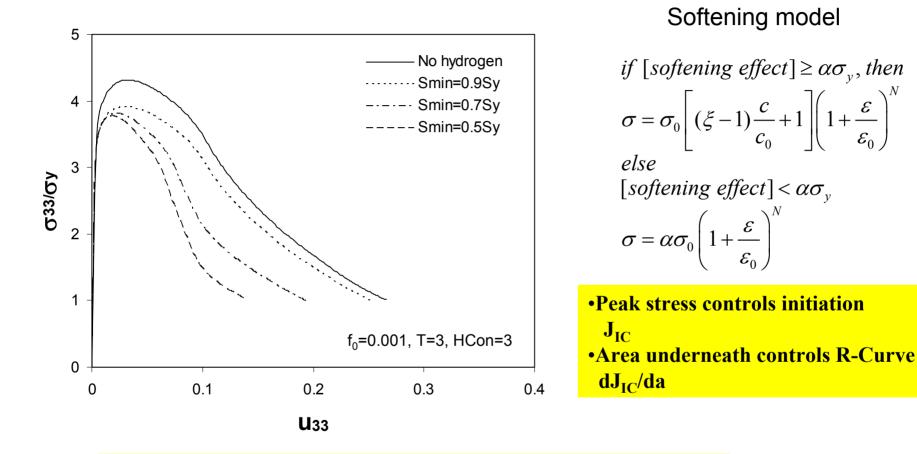


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Material Data for A533B Pressure Vessel Steel



Material Data for A533B Pressure Vessel Steel



without softening: $\sigma_{\max} / \sigma_0 = 4.32$, $\Gamma_0 = 58.2 \text{ kJ/m}^2$ ($D = 200 \mu m$) with softening($\alpha = 0.9$): $\sigma_{\max} / \sigma_0 = 3.91$, $\Gamma_0 = 51.3 \text{ kJ/m}^2(88\%)$ with softening($\alpha = 0.7$): $\sigma_{\max} / \sigma_0 = 3.81$, $\Gamma_0 = 36.8 \text{ kJ/m}^2(63\%)$ with softening($\alpha = 0.5$): $\sigma_{\max} / \sigma_0 = 3.77$, $\Gamma_0 = 27.4 \text{ kJ/m}^2(47\%)$



SUMMARY AND CONCLUSIONS

Hydrogen Embrittlement

- Direct experimental evidence and solid mechanics finite element calculations support the hydrogen enhanced localized plasticity mechanism as a viable mechanism for hydrogen embrittlement
- Indirect experimental evidence, thermodynamic considerations, and ab-initio calculations indicate that hydrogen-induced decohesion can also be a viable mechanism of hydrogen embrittlement

Pipelines

- It appears that do have the capability of assessing whether existing structural material systems can be used for hydrogen transport
- Advanced knowledge and technology are available for the design of new structural materials with hydrogen compatibility

