Hydrogen Embrittlement
Fundamentals, Modeling, and Experiment

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Hydrogen Embrittlement Mechanisms

- Several candidate mechanisms have evolved over the years each of which is supported by a set of experimental observations and strong personal views.

- 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.
Embrittlement and Phenomenology

- Fractographic evidence suggests that low strength steels under static loading fail by
  - Hydrogen-assisted transgranular fracture induced by void or microcrack initiation through decohesion at internal interface (precipitate/inclusion or phase boundaries) ahead of a crack or notch accompanied by shear localization (HELP) leading to the linking of the void/microcrack with the tip of the crack
  - Fracture is controlled by yield strength level and microstructure

- Our contention, which needs to be verified through experiment, is that embrittlement
  - Under static load is a result of the synergistic action of the HELP and decohesion mechanisms
  - Under cyclic load can be intergranular (extremely dangerous mode of failure)
# New Steel Microstructure-Oregon Steel Mills (OSM)

<table>
<thead>
<tr>
<th>API Grade</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
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<th>Ni</th>
<th>V</th>
<th>Nb</th>
<th>Cr</th>
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**acicular ferrite microstructure**

Defects in microstructure, particularly precipitates, act as trap sites for hydrogen

- High dislocation density in some regions
- Irregular grain boundaries and small grains, indicative of microstructure that has not been fully recrystallized and recovered.

Relatively low precipitate density (inside the matrix)
Particle Composition
Energy Dispersive Spectroscopy

- a) EDS spectrum from particle
- b) Bright field TEM image of typical rectangular particle
- c) EDS spectrum from matrix

EDS analysis of fine precipitate inside ferrite grain suggests that precipitate is composed of Ti and Nb

(window detector: C, N, O not detected)
Steel Microstructure-Air Liquide Pipeline

Large intergranular particles (cementite)

Small intragranular particles (carbides with Nb and Ti)
Hydrogen Permeation Measurements

Ultrahigh vacuum (10^-9 torr)
Hydrogen pressure (10 torr)

**Sample**

**Hydrogen Detector**

**Turbo pump**

**Permeability at room temperature**

\[ \Phi = 6.26 \times 10^{12} \frac{\text{H atoms}}{\sqrt{\text{MPa.m.s}}} \]

**Integral of flux (atoms/m²)**

\[ \int J \, dt \]

**Time lag**

\[ t_T = 6.8 \text{ s} \]

\[ t_T = \frac{L^2}{6D_{\text{eff}}} \]

**Oregon Steel Mills sample: thickness**

**L = 120 microns**

**Steady state:**

\[ J_\infty \]

**Pressure:**

\[ P = 4.7 \text{ torr} = 627 \text{ Pa} \]
Thermal Desorption Spectroscopy

\[ d \ln \left( \frac{\Phi}{T_{\text{max}}} \right) = \frac{W_B}{R} \]

\[ d \left( \frac{1}{T_{\text{max}}} \right) \]

\[ W_B = 74.3 \text{kJ/mole} \]

\[ W_B = 70.5 \text{kJ/mole} \]
Materials Characterization

- TEM and TDS
  - will provide the trap binding energy.
- Permeation studies along with numerical simulation of diffusion transients
  - Will validate the trap binding energy determination
  - Will provide the trap density
- Coated samples (SECAT)

- Similar coordinated approach is needed to identify the fracture mechanisms under all loading scenarios
  - Rising load fracture toughness
  - Subcritical crack growth
  - Fatigue
Fracture Mechanics Approach to Design

Determine the stress, deformation, and hydrogen concentration fields ahead of an axial crack in a pipeline.

Case study related to subcritical crack growth experiments carried out at Sandia.
Cracked Pipeline: Problem Statement

\[ C_L(t) = 0 \]

outer diameter: 40.64 cm

thickness: \( h = 9.52 \text{ mm} \)

crack depth: \( a = 1.9 \text{ mm} \)

initial CTOD: \( b_0 = 1.5 \mu\text{m} \)

\( a / h = 0.2 \)

dimensions are in mm

Hydrogen gas at pressure \( P \)

Hydrogen transport

15 MPa

| 15 MPa Hydrogen gas |

\[ J(t) = 0 \]

\[ C_L(t) \propto \sqrt{f} \]

\[ C_L(t) = 0 \]

\[ K : \text{Solubility} \]

\[ J : \text{Hydrogen flux} \]

\[ P : \text{Pressure} \]

\[ f : \text{Fugacity} \]

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Hydrogen Transport Analysis

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

- **Hydrogen populations in NILS and trapping sites are assumed to be in equilibrium according to Oriani’s theory**
  \[
  \theta_T = \frac{\theta_L}{1 - \theta_L} \exp \left( \frac{W_B}{RT} \right)
  \]
  \( W_B = \) Trap binding energy
  \( T = \) Temperature
  \( R = \) gas constant
  - Trap density may evolve dynamically with plastic straining

- **Hydrogen Transport Equation**
  \[
  \frac{D}{D_{\text{eff}}} \frac{dC_L}{dt} = DC_{L,ii} \left( \frac{DV_H}{3RT} C_L \sigma_{kk,i} \right)_{,i} - \alpha \theta_T \frac{\partial N_T}{\partial \varepsilon^p} \frac{d\varepsilon^p}{dt}
  \]
  - Note the effect of stress and plastic strain

\( \theta_L = \) NILS occupany
\( \beta = \) number of NILS per solvent atom.
\( N_L = \) number of solvent atoms/nl.
\( \theta_T = \) trap occupany
\( \alpha = \) number of sites per trap.
\( N_T = \) number of traps/m³.

\( d/dt = \) time differentiation
\( C = \) Hydrogen concentration
\( D = \) diffusion coefficient
\( D_{\text{eff}} = \) Effective diffusion
\( \frac{d}{dC_T} = \) accounting for trapping
\( \sigma_{kk} = \) hydrostatic stress
\( \varepsilon^p = \) plastic strain
\( V_H = \) partial molar volume of H
\( N_T = \) trap density

( )_{,i} = \partial( )/\partial x_i
Material: X70/80 acicular ferrite microstructure

\[ C = K \sqrt{f} \quad f = P \exp \left( \frac{P d}{RT} \right) \quad d = 15.84 \text{ cm}^3/\text{mol} \]

\[ K = 6.54696 \times 10^{18} \frac{\text{H atoms}}{\text{m}^3 \sqrt{\text{Pa}}} \]

\[ C_0 = 2.084 \times 10^{21} \frac{\text{H atom}}{\text{m}^3} \quad P = 1 \text{ atm} \]

\[ C_0 = 2.65932 \times 10^{22} \frac{\text{H atom}}{\text{m}^3} \quad P = 15 \text{ MPa} \]

Lattice diffusion coefficient

\[ D = 1.271 \times 10^{-8} \text{ m}^2/\text{s} \]

Dislocation trapping modeling

\[ N_T = \frac{\sqrt{2} \rho}{a} \quad W_B = 20.2 \text{ KJ/mol} \]

\[ \rho = \begin{cases} 
\rho_0 + \frac{\gamma}{0.15} \varepsilon^p & \varepsilon^p \leq 0.15 \\
\text{const.} & \varepsilon^p > 0.15 
\end{cases} \]

\[ \rho_0 = 10^{10} m^{-2}, \quad \gamma = 10^{16} m^{-2} \]
Hydrostatic Stress at Pressure 15 MPa

Geometric dimensions are in mm
Plastic Strain at Pressure 15 MPa

Geometric dimensions are in mm
Lattice Concentration Toward Steady State

$C_L / C_0$
Lattice Hydrogen Concentration at Steady State

Kumnick and Johnson trapping model

Time to steady-state: 2.0 hrs
\[ t_{ss} = 8 \text{ min } 40 \text{ sec} \]

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

\[ P = 15 \text{ MPa} \]

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Trapped Hydrogen Concentration at Steady State

Kumnick and Johnson trapping model

\[ C_0 = 2.65932 \times 10^{22} \text{ H atom / m}^3 \quad P = 15 \text{ MPa} \]
Total Hydrogen Concentration at Steady State

Kumnick and Johnson trapping model

Time to steady-state is 2.0 hrs

\[ t_{ss} = 8 \text{ min } 40 \text{ sec} \]

\[ \frac{C_L + C_T}{C_0} \]

\[ C_0 = 2.65932 \times 10^{22} \text{ H atom} / \text{m}^3 \quad P = 15 \text{ MPa} \]

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Total Hydrogen Concentration at Steady State

Dislocation trapping model

\[ C_L + C_T \]

\[ C_0 \]

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

\[ P = 15 \text{ MPa} \]

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Full Field (pipeline) vs Boundary Layer Solution (laboratory specimen)

\[ \frac{\sigma_{kk}}{3\sigma_0} \]

Elastoplastic FEM full-field solution \( P = 15 \text{ MPa} \)

Modified Boundary Layer
\[ K_I = 34.12 \text{ MPa} \sqrt{\text{m}} \]
\[ \frac{T}{\sigma_0} = -0.316 \]

\( b = 6.61 \mu \text{m} \)

\( b = 6.31 \mu \text{m} \)

\[ \frac{a}{h} = 0.2 \]

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Full Field (pipeline) vs Boundary Layer Solution (laboratory specimen)

Neglecting the $T$-stress in the MBL formulation fails to predict the true stress

\[
\frac{\sigma_{kk}}{3\sigma_0}
\]

- Elastoplastic FEM full-field solution  $P = 15$ MPa  $b = 6.61 \ \mu m$
- Modified Boundary Layer  $K_I = 34.12 \text{ MPa}\sqrt{\text{m}}$  $T/\sigma_0 = -0.316$  $b = 6.31 \ \mu m$
- Modified Boundary Layer  $K_I = 34.12 \text{ MPa}\sqrt{\text{m}}$  $T/\sigma_0 = 0$  $b = 6.14 \ \mu m$

\[
a/h = 0.2 \quad \frac{R}{b}
\]
Full Field (pipeline) vs Boundary Layer Solution (laboratory specimen)

Full-field solution: \( t_{ss} = 8' : 40'' \)  
MBL approach: \( t_{ss} = 6' : 40'' \)
Fracture Mechanics Assessment

Constraint based fracture mechanics: J-T controlled fracture

Laboratory Specimens

- The deep-notch toughness data in the presence of hydrogen need not necessarily lead to a conservative fracture toughness assessment for shallow cracked geometries as is commonly assumed in the absence of hydrogen

- Shallow crack are attracting hydrogen by plasticity so they, too, are degraded

- Deep-notch cracks are attracting hydrogen by the hydrostatic constraint constraint

Good news

Determine this fracture locus experimentally (Hydrogen effect?)
Modeling the Fracture Process

Transient separation

[ Mishin et al., 2002 ]

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

\(\sigma_{\text{max}}\) : Maximum cohesive stress

\[\kappa = \frac{\text{cohesive energy with } c = 1}{\text{cohesive energy with } c = 0}\]

\[
T_n = \frac{\sigma(c, q) u_n}{q \delta_n}
\]

\[
T_t = \frac{\delta_n \sigma(c, q) u_n}{\delta_t q \delta_t}
\]

\[
q = \sqrt{\left(\frac{u_n}{\delta_n}\right)^2 + \left(\frac{u_t}{\delta_t}\right)^2}
\]
First Principles Calculations

- **Assessment of interfacial strength of second-phase particles in pipeline steels in hydrogen**
  - Ferrite-based alloys have Cr$_{23}$C$_6$ and MnS precipitates at grain boundary 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

- **Calibration of phenomenological parameters in the thermodynamic theory of decohesion of Mishin et al. (200)**

- **Validation of ab-initio calculations for decohesion energy calculations**
  - Unrelaxed binding energies (eV) and their differences for H in Fe grain boundary (GB) and free surface (FS) calculated by VASP PAW-GGA and FLAPW (Zhong et al., 2000).

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<th>GB</th>
<th>FS</th>
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<tr>
<td>Unrelaxed binding</td>
<td>VASP PAW-GGA</td>
<td>-3.23</td>
<td>-3.57</td>
</tr>
<tr>
<td>binding energies</td>
<td>FLAPW GGA (Zhong et al., 2000)</td>
<td>-3.09</td>
<td>-3.42</td>
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Time Scales

\( t_a \): characteristic time of adsorption

\( t_L \): loading rate

\( t_D \): characteristic diffusion time \( \propto \frac{1}{D_{eff}} \)

Effect of time scales on mechanics of crack initiation and growth
Hydrogen Adsorption

\[ \mu = \mu_0(\Theta) + R \Theta \ln(c_L) - \sigma_{kk} V_H / 3 \]

\[ \mu_g = \mu_0(\Theta) + R \Theta \ln(c_{Lg}) \]

\[ c_{Lg} \propto \sqrt{f} \]

\[ \frac{\partial c_L}{\partial t} = \frac{1}{t_a R \Theta} (\mu_g - \mu) \]

\[ t_a : \text{characteristic adsorption time} \]

\[ \frac{\partial c_L}{\partial t} = \frac{1}{t_a} \left[ \ln\left(\frac{c_{Lg}}{c_L}\right) + \sigma_{kk} V_H / 3R \Theta \right] \]

\[ \frac{\partial c_L}{\partial t} = k_c P (c_{Lg} - c_L) \]

\[ (k_c P) t \quad \text{Non-dimensionalized time} \]

\[ \sigma_{kk} = 0 \]

\[ \frac{c_L}{c_{Lg}}(t = 0) = 0.1 \]
WOL Specimen for Subcritical Crack Growth
Finite Element Mesh

Applied displacement

\[ V_0 \]

\[ H = 1.090'' \quad W = 2.240'' \quad B = 2.745'' \]

\[ V_m : \text{Crack mouth opening displacement} \]

\[ \frac{V_m}{2} \]

\[ a \]

Crack tip

\[ W \]

\[ B \]
Comparing FEM Result with ASTM Equation

\[
\frac{K_I}{(V_m E / W^{1/2})} = f(a/W)
\]

\[
E = 220 \text{ GPa}, \quad \nu = 0.3
\]

ASTM \quad f(a/W)

FEM calculations

\[
f(a/W) = \left[1 - a/W\right]^{1/2} \left[ 0.654 - 1.88(a/W) + 2.66(a/W)^2 - 1.233(a/W)^3 \right]
\]

\[a/W\]

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Normalized T-stress for specific $V_m$ – FEM Calculations

$\sigma_0 = 775$ MPa

$V_m = 1$ mm

$\frac{T}{\sigma_0}$

$a / W$

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Plasticity in WOL: Issue of $K$-dominance

\[ V_m = 1.204 \text{mm} \quad \alpha/W = 0.9408 \quad \text{ASTM} \quad K_I = 57.5 \text{ MPa}\sqrt{\text{m}} \]

\[ \text{FEM} \quad K_I = 63.8 \text{ MPa}\sqrt{\text{m}} \]

\[ J = 16008 \text{ N/m} \]

\[ K_I = \sqrt{\frac{JE}{1-V^2}} \]

\[ K_I = 62.2 \text{ MPa}\sqrt{\text{m}} \]
Stresses in WOL: Issue of $K$-dominance

Both $K$- and $J$-dominance

$$\frac{a}{W} = 0.9408 \quad V_M = 1.204\text{mm}$$

- Elasto-plastic solution
- Small Scale Yielding: $K_I = 64\text{ MPa}\sqrt{\text{m}}$
  $T = 249\text{ MPa}$
- Small Scale Yielding: $K_I = 64\text{ MPa}\sqrt{\text{m}}$, $T = 0$
FEM Results for increased load of SNL Exp-2

\[ V_m = 4.9582 \text{mm} \quad a/W = 0.9408 \]

\[ \text{ASTM} \quad K_I = 236.9 \text{ MPa}\sqrt{\text{m}} \]

\[ \text{FEM} \quad K_I = 261.8 \text{ MPa}\sqrt{\text{m}} \]

Loss of both \( K \)- and \( J \)-dominance

\[ J = 124000 \text{ N/m} \]

\[ K_I = \sqrt{\frac{JE}{1-v^2}} \]

\[ K_I = 170 \text{ MPa}\sqrt{\text{m}} \]

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Conclusions and Future Work

- **Hydrogen adsorption and transport methodology**
  - Interaction of time scales
  - Possible effects on remediation

- **Mechanisms of fracture (microstructural characterization)**
  - Material system dependence
    - Steel microstructure
    - Weldment
  - Load mode dependence (static vs fatigue)
  - Mode of hydrogen uptake (subcritical crack growth)

- **Coupling mechanisms with transport to understand**
  - Crack initiation
  - Crack propagation
  - Devise fracture criteria with predicting capabilities
    - Possibly a $J_{IC}-T$ locus

- **Fracture mechanics/mechanism-based approach to design**
  - As opposed to the SMYS approach
Hydrogen-Induced Degradation in 4340 Steel

- Studies on the mechanical properties of high-strength steel (AISI 4340) characterize the marked deterioration in fracture strength with increase in hydrogen concentration.

- Mechanical properties are used in the statistical model of hydrogen-assisted fracture

Results for 4-point Bend Single Notched Specimens: Experiment vs Modeling

- double-notch bend testing shows that without H, fracture is strain-controlled, i.e., initiation occurs at the notch (left)

- with H, fracture is inter-granular and stress-controlled; initiation occurs ahead of the notch (right)
Additional slides
Conclusions on WOL

- Abaqus result on K seems to be correct
  - See comparison with the compact tension specimen which we “assume” has a more accurate calibration function
- We do have K dominance even for a crack of a/w=0.94
  - This is not the case for X-52 at such large a/w
- An important outcome is that we have both K and T. In combination with the experiment we can explore criticality conditions based on two parameter characterization
  - Study the hydrogen effect on this two-parameter characterization
Stress – plastic strain curve

\[ \sigma_e \text{ [MPa]} \]

\[ \varepsilon^p \]
Long Term Objective: Multiscale Fracture Approach

(a) Crack tip fracture process zone
(b) Axisymmetric unit cell model

(c) Traction - separation law

\[ \sigma_{\text{max}} \]

\[ \Gamma \]

Dissipated energy

\[ \sum_{33} \]

\[ u_3 \]

\[ u_1, \Sigma_{11} \]

\[ \sum_{33} \]

\[ c_L^{\text{initial}} \text{ at time}=0 \]

Triaxiality
Hydrogen concentration

(e) Cohesive elements characterized by a traction-separation law based on the unit cell model

Adjacent finite element

With hydrogen softening in
(1) cohesive zone and matrix
(2) cohesive zone only

No hydrogen

\[ J/(\sigma_0 D_0) \]

\[ \Delta a/D_0 \]

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Future Work

- **Other Activities**
  - Finite element analysis of residual stresses of a Schott Coating sitting on the substrate

![Graph showing residual stresses](attachment://stress_graph.png)

- Average tensile stress $\sigma_{\text{II}}$ in the coating is 125 MPa

- Note that substrate is under large compression (-100MPa) at the edges (possible delamination cause)

- Continue collaboration with ASME on establishing guidelines for codes and standards

- Continue our ongoing collaboration with the Japan program for materials solutions for the Hydrogen Economy
  - Hydrogen National Institute for Use and Storage (Hydrogenius)
    - Kyushu University (Prof. Y. Murakami)

- Continue our ongoing collaboration with the NATURALHY Project sponsored by the European Union
  - Interaction of hydrogen in a pipeline with a corrosion induced-crack on the external wall
Future Work

- **Experiment**
  - Establish the diffusion characteristics of existing and new pipeline steel microstructures
    - Existing pipeline steel samples provided by Air Liquide and Air Products. Specimens are in our laboratory
    - New micro-alloyed steels (new microstructures) provided by Oregon Steel Mills through DGS Metallurgical Solutions, Inc.
  - Collaboration with ORNL and Schott North America for coating of our samples
  - Determine uniaxial tension macroscopic flow characteristics in the presence of hydrogen
  - Carry out fracture testing: Collaboration with Sandia, Livermore
  - SEM and TEM studies on existing and new pipeline material microstructures
    - Fracture surfaces, particle, dislocation, and grain boundary characterization

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<tr>
<td>D X52/60</td>
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<td>0.24</td>
<td>0.14</td>
<td>0.001</td>
<td>0.084</td>
<td>0.16</td>
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Typical natural gas pipeline steel
- Ferrite/acyicular ferrite
- Ferrite/acyicular ferrite
- Ferrite/low level of pearlite

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Additional slides
Critical Assumptions and Issues

- Hydrogen-induced cracking in existing pipeline steels initiates at second phase particles by hydrogen-induced decohesion followed by shear localization of ligaments
  - Fracture toughness testing and SEM/TEM studies will verify this assumption

- Embrittlement of acicular ferrite initiates at the needle-pearlite/ferrite interface
  - Fracture toughness testing and SEM/TEM studies will verify this assumption

- Hydrogen dramatically degrades the resistance of steel to fatigue crack growth. Possible remediation by water vapor and oxidation
  - Experiments to study the oxidation effects

- Lack of funding does not allow
  - Hire personnel
  - Construct experimental devices
  - Carry out testing

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Ahead of the crack tip

\[ \frac{\sigma_{kk}}{3\sigma_0} \]

- Elastic FEM pipeline geometry \( P = 15 \text{MPa} \)
- Asymptotic Solution \( K_I = 34.12 \text{ MPa}\sqrt{m} \)
- \( T / \sigma_0 = -0.316 \)
- Elastoplastic FEM pipeline geometry \( P = 15 \text{MPa} \)

\( \sigma_0 = 595 \text{ MPa} \)

\[ R \quad (\mu \text{m}) \]

\[ b \]

- 11% reduction
- 6% reduction

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EDS reference

EDS of gold sample showing copper peaks from sample holder
Permeation

- Ultrahigh vacuum (10^-9 torr)
- Hydrogen pressure (10 torr)

- Hydrogen is introduced on one side of the sample
- Permeates through sample
- Detected by ion pump

- 4.75 cm disks
- 100 micron thickness
- Palladium coating on exit side
- Testing coatings on hydrogen side

Real-world pipeline specimens are in our possession for testing. Air Liquide and Air Products provided the coupons.
Transient to Steady State - Lattice Concentration

$C_L / C_0$
**Full Field (pipeline) vs Boundary Layer Solution (laboratory specimen)**

\[
\frac{C_L}{C_0} = \frac{\sigma_{kk}}{3\sigma_0}
\]

- Crack length of 1.9 mm \( a/h = 0.2 \), \( b = 6.61 \, \mu m \)
- Crack length of 0.476 mm \( a/h = 0.05 \), \( b = 1.06 \, \mu m \)

\[
\begin{align*}
a/h &= 0.2 \\
K_I &= 34.12 \, MPa\sqrt{m} \\
T/\sigma_0 &= -0.316
\end{align*}
\]

\[
\begin{align*}
a/h &= 0.05 \\
K_I &= 14.38 \, MPa\sqrt{m} \\
T/\sigma_0 &= -0.292
\end{align*}
\]

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Fracture Assessment

From the full pipeline to laboratory specimens

Crack depth/pipeline thickness
Hydrogen effect on ductile crack growth

- crack growth mechanisms
  - Void by void growth
  - Multiple void growth

\[ f_0 = \pi \left( \frac{R_0}{X_0} \right)^2 \]

- Effect of hydrogen softening and dilatation
- Identifying the range of \( f_0 \) that each mechanisms is operative

[ Tvergaard and Hutchinson, 2002
Petti and Dodds, 2005]
Ab-initio

- We have completed several necessary validation “computer experiments” on the binding energies for H in Fe grain boundary and free surface using a pseudopotential based plane-wave method via projected-augmented wave basis functions, as implemented in the Vienna \textit{ab initio} Simulation Package. A subset of our validation results provides unrelaxed binding energies for H in Fe for GB/FS equal to -3.23/-3.57 eV, and the binding energies difference of the GB and FS equal to +0.34 eV, in good agreement with values in literature [4].
Ahead of the crack tip at steady state

Kumnick and Johnson (1980) trapping model

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

- \( \varepsilon^p \)
- \( \sigma_{kk} / 3\sigma_0 \)
- \( C_L / C_0 \)
- \( C_T / C_0 \)
- \( (C_L + C_T) / C_0 \)

\( L = 0.3'' \) uncracked ligament

\[ L: \text{uncracked ligament} \quad x / L \]
Compact Tension Specimen: FEM Result vs Handbook

\[
\frac{K_I}{(P/\sqrt{W})} = f \left( \frac{a}{W} \right) = \frac{2 + \frac{a}{W}}{\left( 1 - \frac{a}{W} \right)^{3/2}} \left[ 0.886 + 4.64 \left( \frac{a}{W} \right) - 13.32 \left( \frac{a}{W} \right)^2 + 14.72 \left( \frac{a}{W} \right)^3 - 5.6 \left( \frac{a}{W} \right)^4 \right]
\]

\( f \left( \frac{a}{W} \right) \)

Tada, et al.

FEM calculations

\( E = 220 \text{ GPa} \), \( \nu = 0.3 \)