Hydrogen-Assisted Fracture: Materials Testing and Variables Governing Fracture

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Livermore, CA

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SNL has 40+ years experience with effects of high-pressure hydrogen gas on materials

- Design and maintenance of welded stainless steel pressure vessels for containment of high-pressure H$_2$ isotopes
  - Extensive testing of stainless steels exposed to high-pressure H$_2$ gas
- Six-year program in 1970s focused on feasibility of using natural gas pipeline network for H$_2$ gas
  - Materials testing in high-pressure H$_2$ gas using laboratory specimens and model pipeline
  - Examined fusion zone and heat affected zones of welds
- Active SNL staff have authored 70+ papers and organized 6 conferences/symposia on H$_2$ effects in materials
  - Seventh conference on Hydrogen Effects on Material Behavior scheduled for Sept. 2008 at Jackson Lake Lodge, Wyoming
SNL/CA has capabilities for producing both strength of materials and fracture mechanics data.

**Strength of Materials:**

- \( \sigma_{UTS} \)
- \( \sigma_{YS} \)
- \( \varepsilon_f \)
- RA

\[ \frac{d\delta}{dt} > 0 \]

**Fracture Mechanics:**

- \( K_{IH} \)
- \( K_{TH} \)

\[ \frac{d\delta}{dt} \geq 0 \]

\[ \delta = \text{constant} \]
Thermal charging of specimens in H$_2$ gas

- Two high-temperature charging stations
  - temperatures up to 300 °C (572 °F)
  - pressures up to 138 MPa (20 ksi)
  - two to four A286 primary vessels in 304 secondary containment
  - H concentrations from 7,000 to 15,000 appm in stainless steels

- Specimens
  - compact tension and 3-pt bend fracture mechanics ($K_{IH}$)
  - smooth and notched tensile ($\sigma_{UTS}$, $\sigma_{YS}$, $\varepsilon_f$, RA)

- Dedicated 90 kN (20 kip) servo-hydraulic load frame for rising displacement testing
Measurement of $K_{TH}$ in high-pressure $H_2$ gas

- Five stations for testing in high-pressure $H_2$ gas
  - pressures up to 200 MPa (29 ksi)
  - room temperature
  - A286 primary vessels in 304/321 containment
Measurement of $K_{TH}$ in high-pressure $H_2$ gas: instrumented WOL and DCB specimens

- **WOL specimens**
  - procedures follow ASTM E1681-99
  - constant displacement with instrumented load cell
  - strain gages yield load vs. time:
    - crack advance $\rightarrow$ load drop $\rightarrow$ $K$ drop
  - crack arrests when $K = K_{TH}$ (load constant with time)

- **DCB specimens**
  - procedures follow NACE TM0177-96
  - constant displacement from wedge
  - strain gage signals crack initiation and arrest
  - crack arrests when $K = K_{TH}$ (strain gage signal constant)
Measurement of $K_{TH}$ in high-pressure H$_2$ gas: test assembly

- Up to 4 WOLs in each cradle
  - 2 cradles/vessel
- Up to 8 DCBs in each modified cradle
  - 1 cradle/vessel
- Displacement loading applied in air

Test durations can be 1000+ hours for both stainless steels and ferritic steels
Measurement of $K_{TH}$ in high-pressure H$_2$ gas: environmental chamber

- **Temperatures**
  - +175 °C to -75°C (-347 °F to -103 °F)

- **Pressures**
  - 200 MPa (29 ksi) below room temperature
  - 138 MPa (20 ksi) above room temperature

- **Capacity**
  - one test vessel (8 WOLs or 8 DCBs)
Tensile tests with internal hydrogen

1. Materials
   - Forged 22Cr-13Ni-5Mn and 21Cr-6Ni-9Mn stainless steels
   - Cold-worked and annealed 316 stainless steel
   - Cold-worked and annealed SAF 2507 duplex stainless steel
   - X-70 and X-80 pipeline steels

strain-hardened bar stock
H-precharging = 138 MPa H₂, 573 K, 10 days
1- tested in air
2- H-precharged, tested in air

Stress, $S_y, S_u$ (MPa)

Elastic modulus, $E_{tu}$

Plastic strain, $\Delta \delta / \Delta t > 0$

$H$-precharging = 138 MPa H₂, 573 K, 10 days

Ductility, RA (%)

- $1$- tested in air
- $2$- H-precharged, tested in air
Fracture toughness tests with internal hydrogen

22-13-5 forgings
CT specimens
longitudinal
25°C

Materials
- Forged 22Cr-13Ni-5Mn and 21Cr-6Ni-9Mn stainless steels
- Cold-worked 316 stainless steel
- Cold-worked SAF 2507 duplex stainless steel
- Stainless steel welds
Calculations involving high-pressure H₂ must consider fugacity

\[ f = P \exp\left(\frac{bP}{RT}\right) \]

\[ b = 15.55 \text{ cm}^3/\text{mol} \]

\[ \chi = K_o \exp\left(\frac{-\Delta H_s}{RT}\right) f^{1/2} \]

\[ J_\infty = \frac{\Phi_o \exp\left(\frac{-H_\Phi}{RT}\right)}{l} f^{1/2} \]
Crack growth threshold tests in hydrogen gas

Quenched and tempered low-alloy steels

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM 4340</td>
<td>1.81</td>
<td>0.84</td>
<td>0.27</td>
<td>0.41</td>
<td>0.82</td>
<td>0.29</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>AM 4340</td>
<td>1.71</td>
<td>0.82</td>
<td>0.21</td>
<td>0.41</td>
<td>0.75</td>
<td>0.22</td>
<td>0.007</td>
<td>0.012</td>
</tr>
<tr>
<td>SA 372 Gr. J</td>
<td>-</td>
<td>0.96</td>
<td>0.18</td>
<td>0.48</td>
<td>0.92</td>
<td>0.30</td>
<td>0.002</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Summary of tests

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_{YS}$ (MPa)</th>
<th>$H_2$ (MPa)</th>
<th>$K_o$ (MPa√m)</th>
<th>$K_{TH}$ (MPa√m)</th>
<th>Initiation time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM 4340</td>
<td>862</td>
<td>100</td>
<td>40-60</td>
<td>29-34</td>
<td>65</td>
</tr>
<tr>
<td>VM 4340</td>
<td>862</td>
<td>40</td>
<td>40-60</td>
<td></td>
<td>&gt;500</td>
</tr>
<tr>
<td>VM 4340</td>
<td>600</td>
<td>100</td>
<td>50-75</td>
<td></td>
<td>&gt;350</td>
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<tr>
<td>VM 4340</td>
<td>600</td>
<td>40</td>
<td>70-80</td>
<td></td>
<td>&gt;500</td>
</tr>
<tr>
<td>AM 4340</td>
<td>828</td>
<td>100</td>
<td>40-60</td>
<td></td>
<td>&gt;5000</td>
</tr>
<tr>
<td>AM 4340</td>
<td>828</td>
<td>130</td>
<td>40-60</td>
<td>35-37</td>
<td>1800</td>
</tr>
<tr>
<td>SA 372 Gr. J</td>
<td>718</td>
<td>80</td>
<td>35-105</td>
<td></td>
<td>&gt;5000</td>
</tr>
</tbody>
</table>
$K_{TH}$ measurements for 4340 compared to literature data

Initial $K_{TH}$ measurements for modern “clean” steels are similar to data for older steels

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**Pressure Vessel Steels**

- **4147 steel ($\sigma_{YS}=869$ MPa [126 ksi])**
- **4147 steel ($\sigma_{YS}=780$ MPa [113 ksi])**

Data from Loginow and Phelps, *Corrosion*, 1975

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Diagrams showing $K_{TH}$ measurements versus $H_2$ gas pressure for different steels.
Complications testing pressure vessel steels

- Time for initial crack extension in $\text{H}_2$ gas varies widely
  - 65 hrs for VM 4340 vs >5000 hrs for AM 4340 in same test vessel
  - $\text{H}_2$ gas purity important
  - surface oxides important
    - WOL and DCB specimens displacement loaded in air
  - Nelson, *ASTM STP 543*, 1974 → $\text{H}_2$ dissociation may govern crack extension in 4130 steel

- Long cracks complicate $K_{\text{TH}}$ measurement in constant-displacement tests
  - $a/W \geq 0.8$ in VM 4340 WOL specimens
# H₂ gas analysis in crack growth system

## Gas sampling after H₂ flow through manifold

<table>
<thead>
<tr>
<th></th>
<th>O₂ (ppm)</th>
<th>H₂O (ppm)</th>
<th>N₂ (ppm)</th>
<th>CO (ppm)</th>
<th>CO₂ (ppm)</th>
<th>THC (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.9999% H₂ spec.</td>
<td>&lt;0.05</td>
<td>&lt;0.5</td>
<td>&lt;0.2</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>manifold</td>
<td>0.2</td>
<td>&lt;0.5</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>manifold + mol. sieve</td>
<td>0.5</td>
<td>&lt;0.5</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

## Gas sampling after H₂ flow through manifold + pressure vessel

<table>
<thead>
<tr>
<th></th>
<th>O₂ (ppm)</th>
<th>H₂O (ppm)</th>
<th>N₂ (ppm)</th>
<th>CO (ppm)</th>
<th>CO₂ (ppm)</th>
<th>THC (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.9999% H₂ spec.</td>
<td>0.1</td>
<td>0.16</td>
<td>0.32</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>manifold + vessel</td>
<td>0.3</td>
<td>2</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

## Gas compositions from other laboratories

<table>
<thead>
<tr>
<th></th>
<th>O₂ (ppm)</th>
<th>H₂O (ppm)</th>
<th>N₂ (ppm)</th>
<th>CO (ppm)</th>
<th>CO₂ (ppm)</th>
<th>THC (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loginow &amp; Phelps</td>
<td>&lt;5</td>
<td>50</td>
<td>1000</td>
<td>n/a</td>
<td>&lt;10</td>
<td>n/a</td>
</tr>
<tr>
<td>Walter &amp; Chandler</td>
<td>&lt;0.2</td>
<td>~1</td>
<td>0.6-0.9</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>
Preclude surface oxide effect with glovebox

Loading crack in air

Exposure to hydrogen gas

Loading crack in glovebox

Exposure to hydrogen gas
Long cracks result in elevated $K_{TH}$ measurements

$K_{TH} = K_{meas} + K_{cl}$

Measured load vs. COD for WOL specimens

<table>
<thead>
<tr>
<th>4340 specimen</th>
<th>Initial $K$ (MPa√m)</th>
<th>$K_{TH}$ (MPa√m) meas. load</th>
<th>$K_{TH}$ (MPa√m) minus closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM (BC)</td>
<td>61</td>
<td>56</td>
<td>34</td>
</tr>
<tr>
<td>VM (BD)</td>
<td>43</td>
<td>46</td>
<td>29</td>
</tr>
<tr>
<td>AM (AC)</td>
<td>40</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>AM (AD)</td>
<td>62</td>
<td>47</td>
<td>35</td>
</tr>
</tbody>
</table>
$H_2$-assisted fracture depends on environment: hydrogen source

H₂-assisted fracture depends on **environment:** gas purity

Data from: H.H. Johnson, *Fundamental Aspects of Stress Corrosion Cracking*, 1967

Data from: M.O. Speidel, *Hydrogen Embrittlement and Stress Corrosion Cracking*, 1984
H$_2$-assisted fracture depends on environment: gas purity

- Impurities such as O$_2$ preferentially adsorb on clean metal surfaces → inhibits adsorption of H$_2$
  - limits H uptake at crack tip
- Effect of O$_2$ may depend on absolute partial pressure
  - effect of O$_2$ may be observed at lower concentrations for higher H$_2$ pressures
- Other impurities may have same effect as O$_2$
  - SO$_2$, CO, CS$_2$, CO$_2$

- Resource: *ASTM STP 543*, 1974
H$_2$-assisted fracture depends on **material: composition**

\[
\text{4340 (} \sigma_{YS} = 1450 \text{ MPa)}
\]

Data from: N. Bandyopadhyay et al., *Metallurgical Transactions A*, 1983
SUMMARY

• SNL can characterize hydrogen effects on materials using strength of materials and fracture mechanics approaches
  - thermal charging of test specimens using high-pressure H₂
  - static loading of test specimens in high-pressure H₂
• SNL has active programs testing materials in high-pressure H₂
  - pressure vessel steels and stainless steels
• Numerous variables impact hydrogen-assisted fracture of structural materials
  - environmental variables
  - material variables
  - mechanical variables