Hydrogen Effects in Materials

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Outline

- **Introduction**
  - $\text{H}_2$ interactions with metal components
  - Safety concern: *hydrogen embrittlement* (HE)

- **Methods to assess material performance**

- **Variables affecting HE**
  - *Material*
  - Environmental
  - Mechanical
Outline

• Considerations for materials selection

• Component design
  - Design approach
  - Material property measurement
  - Example design analysis

• Recommendations
H₂ containment components

On-board fuel tanks

Manifold components
$\text{H}_2$ containment components

Transport and stationary tanks

Pipelines
H₂ interactions with metal components

1) H₂ gas
2) H₂ adsorption
3) H₂ dissociation to H
4) H absorption
5) H diffusion
Two principal safety concerns

• **H\textsubscript{2} permeation** through wall of structure  
  - Effectively results in H\textsubscript{2} leak

• **Hydrogen embrittlement (HE)** of structural metal  
  - Crack propagation through wall of structure  
  - HE mechanisms involve H in solution  
    • Temperatures < 200 \textdegree C  
    • Other H-related degradation mechanisms operate >200 \textdegree C
HE enables crack propagation

Component surface

Stress

Defect

H absorbs into surface

H concentrates at defect

H causes embrittlement and crack propagation

H causes embrittlement and crack propagation
Hydrogen embrittlement mechanisms

Hydrides
D. Westlake, H. Birnbaum

Hydrogen-Enhanced Localized Plasticity (H.E.L.P.)
C. Beachem, H. Birnbaum, I. Robertson, P. Sofronis

Hydrogen-Enhanced Decohesion
A. Troiano, R. Oriani
HE due to hydrogen-enhanced decohesion

“Intergranular” HE can be devastating

Barthélémy, 1st ESSHS, 2006
Material performance: test methods

**Strength of materials:**
- \( \sigma_u, \sigma_y, \varepsilon_f, \text{RA} \)
- S-N

**Fracture mechanics:**
- \( K_{IH}, K_{TH} \)
- \( \text{da/dN vs } \Delta K \)

\[ \frac{dl}{dt} > 0 \]

\[ \frac{d\delta}{dt} \geq 0 \]
Material performance: test methods

HE manifested by reduced fracture toughness
HE manifested by increased fatigue crack growth rate

X42 ferritic steel
frequency = 1 Hz

1000 psi H₂, R=0.1
1000 psi N₂, R=0.1

Cialone and Holbrook,
Met Trans A, 1985
Material performance: service experience

- Fuel tanks
  - *Aluminum* or polymer lined composite
  - $\text{H}_2$ pressure $< 70$ MPa

- Manifold components
  - *Austenitic stainless steel*
  - $\text{H}_2$ pressure $< 138$ MPa
  - Low material strength
  - No welds
Material performance: service experience

• Storage tanks
  - Low-alloy ferritic steel
  - H₂ pressure < 42 MPa
  - Limited material strength
  - No welds

• Pipelines
  - C-Mn ferritic steel
  - H₂ pressure < 14 MPa
  - Low material strength
  - No pressure cycling
H₂ compatibility guidelines for metals

• Materials favored for H₂ service
  - austenitic stainless steels, aluminum alloys, low-alloy ferritic steels, C-Mn ferritic steels, copper alloys

• Materials commonly avoided in H₂ service
  - high-alloy ferritic steels, nickel alloys, titanium alloys

HE susceptibility can be sensitive to many variables
Variables affecting HE

• All metals can be susceptible to HE depending on
  - Material variables
  - Environmental variables
  - Mechanical variables

• Trends demonstrated from laboratory test methods
  - Emphasize fracture mechanics data
  - Emphasize ferritic steels, austenitic stainless steels, aluminum
Material variable: strength (hardness)

Pressure Vessel Steels
H₂ gas pressure = 41 MPa

Yield strength (ksi)

<table>
<thead>
<tr>
<th>Yield strength (ksi)</th>
<th>KₜH (ksi-in¹/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>105</td>
<td>110</td>
</tr>
<tr>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>135</td>
<td>90</td>
</tr>
<tr>
<td>150</td>
<td>80</td>
</tr>
</tbody>
</table>

Pressure Vessel Steels
H₂ gas pressure = 41 MPa

- 4130 steel
- 4145 steel
- 4147 steel

Strength promotes HE in all materials

Technologically important trend

Loginow and Phelps, *Corrosion*, 1975
Material variable: alloy composition

Alloy composition affects intergranular HE in ferritic steels

Ni-Cr-Mo ferritic steel
\( \sigma_{YS} = 1450 \text{ MPa} \)
110 kPa H\(_2\) gas
296 K

Bandyopadhyay et al., *Met Trans A*, 1983
Material variable: alloy composition

Nickel affects deformation and/or martensite formation in stainless steels

San Marchi et al., *IJHE*, 2008
Material variable: welding

- Weld microstructure can promote HE
- Hardness, residual stress also affect HE
Environmental variable: $H_2$ pressure

$d\delta/dt \geq 0$

Pressure Vessel Steels
- 4130 steel ($\sigma_{YS}=634$ MPa)
- 4145 steel ($\sigma_{YS}=669$ MPa)
- 4147 steel ($\sigma_{YS}=724$ MPa)

Loginow and Phelps, *Corrosion*, 1975

HE more severe at higher $H_2$ pressure for all materials
Environmental variable: temperature

HE can be maximum at ambient temperature

Gas impurities can inhibit or intensify HE in ferritic steels
Environmental variable: $H_2$ purity

Water vapor promotes HE in aluminum alloys

Speidel, *Hydrogen Embrittlement and Stress Corrosion Cracking*, 1984
**Mechanical variable: loading rate**

<table>
<thead>
<tr>
<th>Loading rate, $dK/dt$ (MPa·m$^{1/2}$/min)</th>
<th>$K_{IH}$ (MPa·m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
</tr>
</tbody>
</table>

4340 ferritic steel

$\sigma_{YS} = 1235$ MPa

550 kPa H$_2$ gas

297 K

HE more severe at lower loading rates in all materials

Clark and Landes, ASTM STP 610, 1976
Mechanical variable: load cycle frequency

CASE 105 ferritic steel
103 MPa H₂ gas
load ratio = 0.1

ΔK (MPa-m^{1/2})

da/dN (μm/cycle)

0.1
1
10
100

0 1 5 0 4 5 6 0

0.01 Hz
0.1 Hz
1.0 Hz


HE more severe at lower load cycle frequency in all materials
Considerations for materials selection

1) HE data or service experience should not be extrapolated

- \( \text{H}_2 \) compatibility must be established for specific conditions
Considerations for materials selection

2) HE can be severe in alloys considered compatible with H₂

- Intersections of variables important
3) Materials selection may balance H₂ compatibility with other constraints

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost</th>
<th>Specific strength</th>
<th>Temperature range</th>
<th>HE resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>austenitic SS</td>
<td>high</td>
<td>low to high</td>
<td>cryogenic to high</td>
<td>high</td>
</tr>
<tr>
<td>C-Mn/low-alloy steels</td>
<td>low</td>
<td>low to high</td>
<td>ambient to high</td>
<td>low to intermediate</td>
</tr>
<tr>
<td>aluminum</td>
<td>intermediate</td>
<td>intermediate to high</td>
<td>cryogenic to low</td>
<td>high</td>
</tr>
</tbody>
</table>
Considerations for materials selection

4) Materials must be qualified for $H_2$ service based on

- Material property measurements under relevant conditions
  - Material variables
  - Environmental variables
  - Mechanical variables
- Design approach for component
Design based on fracture mechanics

Local stress drives crack extension

\[ \sigma_{\text{local}} = \sigma_c \]
Design based on fracture mechanics

\[ \sigma_{ij} = \frac{K}{\sqrt{2\pi r}} f_{ij}(\theta) \]

- Local stress described by stress-intensity factor, K
- Crack extension governed by critical K values
Component design: sustained-load cracking

H₂ induces time-dependent crack propagation under static loading
Component design: sustained-load cracking

Sustained-load cracking proceeds when $K > K_{TH}$

$$K = p \times f(a/t, R_i, R_o)$$

$K_{TH}$ measured in laboratory

Sustained-load cracking proceeds when $K > K_{TH}$
Component design: fatigue crack growth

Crack growth under cyclic loading accelerated by $H_2$

Number of pressure cycles, $N$ (time = $N/f$)

Crack in $H_2$

Crack in $N_2$
Fatigue crack growth rates \((\frac{da}{dN})\) are a function of \(\Delta K\):

\[
\Delta K = \Delta p \times f(a/t,R_i,R_o)
\]

\[
\frac{da}{dN} = C[\Delta K]^m
\]

Component design: fatigue crack growth
Component design analysis

- Objective: calculate number of pressure cycles, $N_c$, to grow crack to critical length, $a_c$

$$K = p \times f(a/t,R_i,R_o)$$

critical crack depth for sustained-load cracking

cycles to critical crack depth

Calculation requires material property measurements: $K_{TH}$ and $da/dN$ vs $\Delta K$
Measurement: fatigue crack growth

d\delta/dt > 0

H2
H2 H2 H2 H2
H2

Sandia National Laboratories
Measurement: fatigue crack growth

\[ \frac{da}{dN} = C [\Delta K]^m \]

SA 105 ferritic steel
103 MPa H₂ gas
load ratio = 0.1

\[ \Delta a = C [\Delta p \ast f(a/t, R_o, R_i)]^m \]

Measurement gives crack length vs number of cycles in design analysis
Measurement: cracking threshold

Wedge Opening Load (WOL) specimen

- Loading bolt
- Load cell

Load (P) vs. Time in H₂

Load (P): $P_0 \propto K_0$

$P_{TH} \propto K_{TH}$
Measurement gives critical crack depth ($a_c$) in design analysis
Example design analysis for H$_2$ pipeline

- **Parameters for H$_2$ pipeline**
  - X42 ferritic steel
  - Inner radius, $R_i = 15$ cm
  - Wall thickness, $t$, from 0.5 to 1.3 cm

- **Maximum pressure**, $p = 10$ MPa

- **Existing defect with depth $a_o$ and length parallel to pipe axis**
Example design analysis for H_2 pipeline

- Case 1: t=0.8 cm (\(\sigma_h=65\% \text{ SMYS}\)) and \(a_o/t=0.10\)
- Case 2: t=1.3 cm (\(\sigma_h=43\% \text{ SMYS}\)) and \(a_o/t=0.10\)
- Case 3: t=1.3 cm (\(\sigma_h=43\% \text{ SMYS}\)) and \(a_o/t=0.05\)
Material/component performance can be quantified with design analysis.
Performance depends on both material properties and component design.

Example design analysis for H₂ pipeline

- **X42 ferritic steel**
  - frequency = 1 Hz
  - da/dN = (2.51 x 10^{-12}) ΔK^{4.56}

- **H₂ gas**
  - pressure cycle = 1 - 10 MPa
  - inner diameter = 30 cm

- **Fatigue crack growth rate**, da/dN (in/cycle)
  - 10^{-8}
  - 10^{-7}
  - 10^{-6}
  - 10^{-5}
  - 10^{-4}
  - 10^{-3}
  - 10^{-2}

- **X42 Pipeline**
  - critical crack depths calculated from K_{TH}

- **Case 1**
  - t = 0.8 cm
  - σₕ = 65% SMYS

- **Case 2**
  - t = 1.3 cm
  - σₕ = 43% SMYS

- **Case 3**
  - t = 1.3 cm
  - σₕ = 43% SMYS

- **Graph**
  - Stress intensity factor range, ΔK (ksi-in^{1/2})
  - number of pressure cycles
Recommendations

1) **Austenitic stainless steels, aluminum alloys** best candidates for H₂ service
   - Based on service experience and testing
   - Do not extrapolate performance or test data
     - Define temperature, alloy composition for austenitic stainless steels
     - Define water vapor content of gas for aluminum alloys
   - Design analysis can quantify safety margins
Recommendations

2) Ferritic steels are susceptible to HE under wide range of conditions
   - Service experience may be adequate but design analysis required in many cases
   - Measure properties under specific conditions
     • Material: strength, alloy composition, fabrication (e.g., welding)
     • Environment: H₂ pressure, H₂ composition, temperature
3) Nickel alloys, titanium alloys are generally not recommended for H\textsubscript{2} service
- Design analysis required
- May require other measures such as H\textsubscript{2} permeation barrier