The Effects of Purity and Pressure on Hydrogen Embrittlement of Metallic Materials (ID 149)
Overview

- Introduction to Hydrogen Embrittlement (HE)
  - Causes and Mechanisms
  - Scope of Research

- Results and Data
  - Test Methods
  - Effects of Pressure
  - Effects of H₂ gas purity

- Issues to Address
Hydrogen Embrittlement in Steels

- Loss of ductility and deformation capacity in the presence of hydrogen
- Strongly affects high-strength steels
- Maximum embrittlement at room temperature (~20°C)
- Causes hydrogen transport by dislocations
Hydrogen Embrittlement in Steels

Factors affecting HE
- Environment
- Material properties and surface condition

Possible Mechanisms of HE
- Stress-induced hydride formation
- Hydrogen-enhanced localized plasticity (HELP)
- Hydrogen-induced decohesion
Environment

- Gas purity
- Pressure
- Temperature
- Exposure time (affects diffusion in internal HE)
- Stress and strain rates
Material Properties related to HE

- Chemical composition of metal
- Heat treatment, welding
- Microstructure
- Cracks, corrosion pits, and other surface defects
Scope of Research

- Metals
  - Carbon, Low alloy, and Stainless Steels
  - Aluminum and Copper

- Focusing on three aspects of HE for steels
  - Effective testing methods for HE
  - Effects of H$_2$ gas pressure (700-1000 bar)
  - Effects of H$_2$ gas purity
Hydrogen Embrittlement

- Austenitic alloys suffer less embrittlement than ferritic alloys
- Martensitic specimens are very sensitive to HE
- Steels often become less ductile, but strength is not significantly reduced by HE
- Aluminum and copper alloys have shown high resistance to HE in tensile testing
TESTING METHODS
Testing for HE

- Need to simulate in-service stresses of pressure vessels -external HE effects

- High sensitivity

- Capable of being reproduced

- Small cells for lower cost and easy cleaning
Tensile Tests

- Compare behavior under pressurized hydrogen vs. inert gas
- Provide data for changes in ductility-elongation and %RA

\[ \% RA = \frac{A_i - A_f}{A_i} \times 100\% \]

- Tensile stresses are uniaxial
Fracture Mechanics

- **Wedge Opening Load (WOL)**
  - Test of threshold stress intensity factor, $K_{TH}$
  - Crack growth Maximum acceptable crack growth: 0.25mm [1]

- **Compact Tension (CT)**
  - Fatigue crack growth rate, $da/dN$
  - $K_{TH}$ Acceptable criteria: $K_{TH} > (60/950) \times R_m$ (MPa-m0.5), where $R_m$ is UTS of metal [1]

- Plane-strain fracture toughness, $K_{IC}$
Disk Tests

- Disk rupture
  - Provides strength comparison in H₂ and He environments
  - Creates triaxial stress state

- Delayed rupture

- Disk fatigue test
  - Good for simulating life of a pressure vessel
EFFECTS OF HYDROGEN GAS PRESSURE
Pressure Effects

- HE generally increases with partial hydrogen pressure

- Some tests showed maximum HE at a certain pressure level
  - ~100 bar for carbon and low alloys where UTS<1000 MPa
  - ~25 bar for AISI 321 stainless steel [2]
HE Test Results

Large ductility loss with increase of hydrogen pressure for carbon steel [3]
HE Test Results – Disk test

- Hydrogen pressure

Influence of H$_2$S partial pressure for AISI 321 steel
## 316 Stainless Steel

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal precharging</th>
<th>Test environment</th>
<th>Strain rate (s⁻¹)</th>
<th>$S_y$ (MPa)</th>
<th>$S_u$ (MPa)</th>
<th>$E_t$ (%)</th>
<th>$E_u$ (%)</th>
<th>RA (%)</th>
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<td>69 MPa H₂</td>
<td></td>
<td>221</td>
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<td>85</td>
<td>70</td>
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<tr>
<td></td>
<td>None</td>
<td>70 MPa H₂</td>
<td></td>
<td>249</td>
<td>566</td>
<td>85</td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>

Successful performance of 316 steel in tensile tests with high pressure hydrogen [4]
Pressure Test Results

Cracking threshold significantly decreases as hydrogen pressure increases for low alloy steel [4]
HE effects on type 4147 appear to level off at pressures higher than 60 MPa [4]
Effects of 52 MPa hydrogen on fatigue crack growth for HY-100 Steel

HY-100 showed significantly increased crack growth rate in 52 MPa hydrogen [4]
In tests performed at 103.4 MPa on SA-105 steel, fatigue crack growth was slower at higher frequencies [5]
Results of High Pressure Tests

- Losses in ductility increase with pressure, although several steels reached maximum embrittlement at a threshold pressure.

- Fracture toughness and resistance to crack propagation decrease.

- Strength of the material is usually not significantly affected.
Effects of High Pressure Hydrogen

- Fatigue resistance decreases at higher pressures
- A286 and 316 stainless steels have shown the most resistance to HE
- Aluminum and copper alloys appear to be resistant to HE
- More fatigue testing at high pressure needs to be performed on these materials
EFFECTS OF HYDROGEN GAS PURITY
# Impurities Affecting HE

<table>
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<tr>
<th>HE Inhibitor</th>
<th>No Effect</th>
<th>Embrittling Effect</th>
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</thead>
<tbody>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;S</td>
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<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
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</table>

H<sub>2</sub>O has demonstrated both embrittling and inhibiting effects.
Impurity Effects

- Oxygen has shown inhibiting effects in delayed disk rupture
- Varying results for impurities such as CH$_4$ and CO$_2$
- H$_2$S has consistently accelerated HE
Effects of gas impurity on HE for carbon steels [4]
Impurity effects on fatigue crack growth

2.25Cr-1Mo steel
S_y = 430 MPa
1.1 MPa H_2 gas
ΔK = 24 MPa√m
frequency = 5 Hz
R = 0.1
293 K

Comparison between pure gas and H_2 with additives [4]
Inhibiting effects of SO$_2$

Sulfur dioxide exhibited inhibitory effects as a pretreatment for steel sheet [6]
Inhibiting effects of oxygen on crack growth in H-11 steel

![Graph showing crack extension in H-11 steel with various conditions.]
Results from Impurity Tests

- $O_2$ consistently acts as an inhibitor
- $H_2S$ has consistently accelerated HE
- Pretreating with $SO_2$ had inhibiting effects during pretreatments
- More data and information is needed regarding purity at higher pressures
Areas for Further Research

- More information needed about threshold pressures at which maximum embrittlement occurs
- Fatigue data for metals demonstrating good HE resistance (A286, 316, Al and Cu alloys)
- More information needed about effects of inhibitors
  - Resolve conflicting claims
  - Specific concentrations for mixtures
  - Inhibiting at higher pressures
## References