Strength properties of steels in high-pressure hydrogen gas and strength design of components

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This work was supported by the New Energy and Industrial Technology Development Organization (NEDO), Fundamental Research Project on Advanced Hydrogen Science (2006 ~ 2012) and Hydrogen Utilization Technology (2013 ~ 2018).

Co-presenters (Kyushu University, Japan)

Prof. Saburo Matsuoka
Prof. Junichiro Yamabe
Topics from 2014 to 2015

TOYOTA brought new FCV "MIRAI" to the market on Dec. 15\textsuperscript{th}, 2014.

HONDA also announced a commercial FCV.

Approx. 50 hydrogen stations will be constructed in 4 regions, Tokyo, Nagoya, Osaka and Fukuoka.
Hydrogen Embrittlement (HE)

Mechanics, Microstructure and Environment

- Plasticity-induced Crack Closure
- Oxide-induced Crack Closure
- Roughness-induced Crack Closure

- Non-propagating Crack → Fatigue Limit

\[ K_{TH} \]

\[ \text{Strength} \approx 1000 \text{ MPa} \]

- Very High Cycle Fatigue
- Hydrogen Embbrittlement Fatigue

Crack Tip Blunting in Air

Crack Tip in H₂

\[ \text{H}_2\text{O}, \text{O}_2, \text{H}_2 \]

Hydrogen Embrittlement

Hydrogen Trapped by Non-metallic Inclusion

Elimination of Fatigue limit

\[ S \]

\[ N \]
INAMORI Frontier Research Center

International Research Center for Hydrogen Energy

Humanity depts. (plan)

I2CNER (2012.11)

HYDROGENIUS (2007.11)

NEXT-FC (2013.5)

JR Kyuudaigakkentoshi Station

Science depts. (plan)

Lens wind turbine

Engineering depts.

Dept. of Hydrogen Energy Systems

Agriculture depts. (plan)

General Undergraduate Education

Hydrogen Station

Reservation zone
## Unique facilities in HYDROGENIUS

![Building with HYDROGENIUS sign](image)

### Fatigue and Fracture Division,
HYDROGENIUS (Research Center for Hydrogen Industrial Use and Storage),
Kyushu University

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#### Material testing machines in high-pressure $H_2$

<table>
<thead>
<tr>
<th>Pressure</th>
<th>~ 120 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test temperature</td>
<td>~45 ~ 120 °C</td>
</tr>
</tbody>
</table>
Fatigue and Fracture Division in HYDROGENIUS

Main research fund

NEDO “Fundamental Research Project on Advanced Hydrogen Science” (2013 ~ 2018)

Aims and scope

• Contribute to revisions of domestic- and international- regulations on material selection and strength design (e.g., design by rule and design by analysis) for components used in high-pressure gaseous hydrogen.

• Elucidate the fundamental principles of hydrogen embrittlement.

• Find and develop new structural materials having higher resistance to hydrogen with lower cost.

Research partners

JPEC, KHK, AIST, NIMS

Material testing machine (~120 MPa H₂)
Two RCN projects including Japan-Norway cooperation on hydrogen degradation research.

**HIPP, 2014-2017:**
Aims to develop a model framework which describes and couples hydrogen degradation mechanisms at different length and time scales towards a predictive mechanism-based integrity assessment.

Norwegian research partners: SINTEF, NTNU, UiO
International res. partners: I²CNER, Bochum University
Industrial Advisory group: Statoil, Aker Solutions, DNV GL

**ROP, 2014-2018:**
A separate work package on hydrogen assisted cracking, specifically addressing resistance towards cracking of the interface between clad and pipeline steel/weld metal.

Norwegian res. partners: SINTEF, NTNU, IFE
Industry partners: Statoil, Gassco, Technip, EDF Induction, POSCO
International collaboration: I²CNER
Slow Strain Rate Tensile (SSRT) testing of stainless steels

Type 316L (17.64Cr-12.22Ni, mass%)

In air, $\phi_{\text{air}} = 87.0\%$
In 78 MPa $H_2$, $\phi_H = 82\%$

$\frac{\sigma_{BH}}{\sigma_{B,\text{air}}} = 0.80$
$\phi_H/\phi_{\text{air}} = 0.37$

Type 304 (18.16Cr-8.15Ni, mass%)

In air, $\phi_{\text{air}} = 87.0\%$
In 83 MPa $H_2$, $\phi_H = 38.3\%$

$\frac{\sigma_{BH}}{\sigma_{B,\text{air}}} = 1.02$
$\phi_H/\phi_{\text{air}} = 0.94$

Fractured specimens
Carbon steels and Cr-Mo steels are categorized as “Extremely” or “Severely” embrittled. Are these materials applicable to the components used in high-pressure H$_2$?
For high-pressure H$_2$, low or moderate strength steels are used (TS < 1000 MPa).
What is the mechanism of HE?
Tensile testing of H-charged low carbon steel SGP

Chemical composition of SGP (mass%)

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.078</td>
<td>0.012</td>
<td>0.35</td>
<td>0.013</td>
<td>0.006</td>
<td>0.12</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Microstructure
(Ferrite-pearlite)

Hydrogen-charging drastically reduced the ductility.

Without hydrogen,
Dimple size: **Small**
(≈ 5 μm in diameter)

With hydrogen,
Dimple size: **Large**
(≈ 10 ~ 20 μm in diameter)

Non-charged

\[ C_{H,R} = 0.01 \text{ mass ppm} \]

H-charged

\[ C_{H,R} = 0.71 \text{ mass ppm} \]
Voids grow in axial direction

$C_{H,R} = 0.01$ mass ppm

Non-charged

Voids grow in lateral direction

$C_{H,R} = 0.71$ mass ppm

H-charged

Effect of hydrogen on microvoid formation

(a) Initiation

Hydrogen concentrates around inclusion by stress-induced diffusion, and therefore localizes slip deformation in the vicinity of inclusion and accelerate the void initiation.

(b) Growth

Hydrogen localize the slip deformation in high-stress zone. In consequence, voids grow in a transverse direction.

(c) Coalescence

Hydrogen facilitates shear fracture between voids, which leads to a ductility loss.

In this case, hydrogen embrittlement can be explained by the hydrogen-enhanced localized plasticity (HELP) model. Namely, the ductility loss is a micro-ductile fracture due to slip localization. (Not embrittlement)

Conclusions for HE in HYDROGENIUS

For the steels with TS < 1000 MPa, the ductility loss under the influence of hydrogen is caused by a micro-ductile fracture due to slip localization, but is NOT caused by the embrittlement of material itself.

We can also use so-called ‘severely embrittled’ materials (e.g., Cr-Mo steels and carbon steels) safely for high-pressure H₂, if we properly understand the mechanism of HE.

Relative tensile strength (RTS) as a function of TS in 69 MPa H₂ gas (NASA database).
Strength design of components used for high pressure $H_2$
Strength design of high-pressure vessels and pipes

Design by Rule (Safety factor: $S=3.5\sim4$)

- e.g. High Pressure Gas Safety Act (Japan)
  - Material selection
  - Determination of wall thickness based on stress analyses

Design by Analysis (Safety factor: $S=2.4$)

- e.g. ASME Sec.VIII Div. 3, EN13445, KHK S 0220
  - Material selection
  - Determination of wall thickness based on stress analyses
  - Analysis for LBB (Leak Before Break)
  - Fatigue life analysis
  - Fatigue crack growth analysis

Wall thickness: $t = a \times \left[ \exp \left( \frac{\sqrt{3p}}{\sigma_{\text{allowable}}} \right) - 1 \right]$

- $\sigma_{\text{allowable}}$: allowable stress
- $\sigma_B$: tensile strength of material
- $p$: allowable pressure
- $a$: inner radius

Safety factor: $S = \frac{\sigma_B}{\sigma_{\text{allowable}}}$

KHK S 0220 (based on ASME Section VIII. Div.3)

“KHK Standard for Pressure Equipments containing Ultra High Pressure Gas” (The High Pressure Gas Safety Institute of Japan)
35 MPa-class hydrogen station ($\approx 2000$)

(1) Design by rule, Safety factor: $S=4$

The requirement for the material: **No embrittlement in H$_2$**
(So-called “Triple set”)
   (i) No degradation in tensile strength, yield strength, elongation and reduction of area in the slow strain rate tensile test in H$_2$ gas
   (ii) No degradation in fatigue strength in H$_2$ gas
   (iii) No degradation in fatigue crack growth in H$_2$ gas

(2) Materials accepted: Type 316L austenitic stainless steel, Cr-Mo steel (JIS-SCM435)*
(JIS-SCM435 was accepted with some conditions.)

70 MPa-class hydrogen station (2010 ~)

(1) Design by rule, Safety factor: $S=4$

Slight embrittlement in H$_2$ was accepted.
   (i) Reduction of area in H$_2$ satisfies a criterion
   (ii) No degradation in fatigue life properties in H$_2$

(2) Materials accepted: Type 316 (hi-Ni), SUH660 (A286), 6061-T6
*Design by analysis with safety factor of 2.4 has also been studied.

In the future, we need to use lower cost materials, such as Cr-Mo steels and carbon steels, which are categorized as “severely embrittled”. 
Fatigue design based on a safety factor

**Design by rule** based on TS

\[
S = \frac{\sigma_B}{\sigma_{\text{allowable}}} = 3.5 \sim 4
\]

Only a stress analysis is required on the basis of the safety factor

ASME Sec.VIII Div. 3, EN13445
KHK S 0220

**Design by analysis** based on TS

\[
S = \frac{\sigma_B}{\sigma_{\text{allowable}}} = 2.4
\]

In addition to the stress analysis, analyses for LBB, fatigue life, FCG etc. are required.

* Instead of \( \sigma_B \), \( \sigma_{\text{flow}} = (\sigma_Y + \sigma_B)/2 \) is sometimes used for design by analysis, where \( \sigma_Y \) is the yield stress.

**Fatigue design of hydrogen-components**

Given the definition of the safety factor \( S \), the tensile strength of material \( \sigma_B \) should not be degraded in hydrogen gas for both the designs. Moreover, in **design by rule** (infinite life design), fatigue limit should not be degraded in hydrogen gas.

**Suggested simple requirements** for **design by rule**:

I. there is no degradation in the tensile strength \( \sigma_B \) in SSRT of smooth specimen, and

II. there is no degradation in the fatigue limit \( \sigma_w \) in smooth specimen, at the maximum design pressure of hydrogen gas.
Strength properties of Cr-Mo steel in high pressure H$_2$
Slow strain rate tensile (SSRT) test in 115 MPa H$_2$

**Specimen**

**SSRT test conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>H$_2$ or N$_2$ (&gt; 99.999 %)</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>115 MPa</td>
</tr>
<tr>
<td>Test temp.</td>
<td>−40 °C, RT, 120 °C</td>
</tr>
<tr>
<td>Crosshead speed</td>
<td>0.002 mm/s (Estimated strain rate) 0.002 mm/s (6.7 × 10$^{-5}$/s)</td>
</tr>
</tbody>
</table>

Max. gas pressure: 120 MPa  
Max. temperature: 120 °C  
Max. frequency: 1 Hz  
Fixing pressure vessel: Press frame
The material showed a remarkable ductility loss in 115 MPa H₂, but showed no degradation in tensile strength.
115MPa N₂ — Fracture morphology in SSRT (JIS-SCM435, RT)

Typical “cup-and-corn” fracture
115MPa H$_2$ — Fracture morphology in SSRT (JIS-SCM435, RT)

The cracks were observed only at the necked part. → The cracks were initiated after starting the non-uniform deformation (necking process)?
Fatigue life testing in 115 MPa H₂

### Fatigue test conditions

<table>
<thead>
<tr>
<th></th>
<th>H₂ or Air (&gt; 99.999 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td></td>
</tr>
<tr>
<td>Gas pressure</td>
<td>115 MPa (H₂)</td>
</tr>
<tr>
<td>Test temp.</td>
<td>RT</td>
</tr>
<tr>
<td>Frequency</td>
<td>1 Hz</td>
</tr>
<tr>
<td>Stress ratio</td>
<td>−1</td>
</tr>
</tbody>
</table>

Servo hydraulic fatigue testing machines

- Max. gas pressure: 120 MPa
- Max. temperature: 120 °C
- Max. frequency: 1 Hz
- Fixing pressure vessel: Press frame
S-N properties of Cr–Mo steel JIS-SCM435

- Degradation of fatigue life due to hydrogen in shorter cycle regime (e.g. $N_f < 10^5$)
- No degradation of fatigue life in longer life regime (e.g. $N_f > 10^5$).
- **No degradation of fatigue limit due to hydrogen** → Design by rule

**Graph Details**
- **HV = 256**
- **Stress amplitude, $\sigma_a$ [MPa]**
- **Number of cycles to failure, $N_f$ [cycles]**
- **Fatigue limit in H₂ gas**
  - $0.5\sigma_B (412\text{MPa})$
  - $0.4\sigma_B (330\text{MPa})$
- **Stress parameters**
  - SCM435 at RT
  - $\sigma_B = 824\text{MPa}$
  - Smooth specimen
  - $f = 1\text{ Hz}$
  - $R = -1$
- **Environmental conditions**
  - 1Hz in H₂ *1
  - 0.1Hz in H₂ *1
  - 0.01Hz in H₂ *1
  - 1Hz in Air

*1: Gas pressure=115MPa
↓ Fatigue limit in H₂ gas

**Stress-Amenity Chart**
- *x-axis*: Number of cycles to failure, $N_f$ [cycles]
- *y-axis*: Stress amplitude, $\sigma_a$ [MPa]
- *graph elements*: Various markers for different environmental conditions and stress amplitude levels.
Fatigue crack growth testing in air and H₂

Materials tested
Cr-Mo steel JIS-SCM435

CT specimen

Test procedure
- Mirror polishing of CT specimen
- FCG test in air or H₂
  \( \rho_{H₂}: 0.7, 10, 40 \) and \( 90 \) MPa
- Observation of slip deformation on the surface of CT specimen
- SEM observation

ASTM E647
- \( \Delta K \)-increasing (\( \Delta P \)-constant) test
- \( \Delta K \)-constant (\( \Delta P \)-decreasing) test

Cr-Mo steel JIS-SCM435: $da/dN - \Delta K$ ($\Delta P$-constant test)

Low $\Delta K$ regime: $(da/dN)_{H2}/(da/dN)_{air}$ was increased with an increase in $\Delta K$.

High $\Delta K$ regime: $(da/dN)_{H2}$ was parallel to $(da/dN)_{air}$.

There were upper bounds of acceleration at $p_{H2}$ of 0.7 ~ 90 MPa.

The existence of the upper bound allows for the provision of a fatigue life estimation for the worst case scenario. → Design by analysis

Pressure cycle tests for vessels

Pressure range: 0.6 ⇔ 45 MPa H₂ gas
Test temperature: Room temperature
Test frequency: 0.006 Hz
Fracture behavior of pressure vessels after cycle tests

Through-wall crack (Pressure vessel A-2, $b = 18$ mm, $t = 25.5$ mm)

(a) No loading
(b) 20-MPa nitrogen gas

LBB failure occurred

Trough-wall crack (Pressure vessel B-2, $b = 24$ mm, $t = 30$ mm)

(a) No loading
(b) 15-MPa nitrogen gas

LBB failure occurred
A series of observation revealed that the ductility loss and fatigue crack growth acceleration (so-called hydrogen embrittlement) are caused by a microscopically ductile fracture, and is NOT "embrittlement" of material itself, even in carbon steels and Cr-Mo steels.

For such materials, both the design by rule and design by analysis can be applicable even for high-pressure hydrogen up to 115 MPa.

In order to achieve both the safety and economic efficiency in Hydrogen Society in the future, the use of lower cost materials with higher susceptibility to hydrogen (e.g., Cr-Mo steels and carbon steels) is necessary.
Thank you for your kind attention.