Effects of dissolved hydrogen and surface condition on the environmentally assisted cracking of 316 stainless steel in PWR primary water

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Outline

• Background introduction
• Materials and experimental
• Results and discussion
• Conclusions
Background

- In BWRs, hydrogen is added to the water to maintain a low dissolve oxygen levels/low electrochemical potential and minimized the oxidation rate and the intergranular stress corrosion cracking (IGSCC). (W. Bilanin, et al., Progress in Nuclear Energy, 20 (1987) 43-70)
- However, in the primary water of PWRs, several studies have shown that the hydrogen in the solution increased the oxidation rate but decreased the crack growth rate. (Corrosion Science, 53 (2011) 2558-2565.)
- The oxidation analysis of Stainless steel and Fe-Cr demonstrated, “the oxidation rate is higher when hydrogen is present in the metal”. (D. Wallinder et al., J. Electrochem. Soc., 2002; E. Essuman et al., Oxid. Met., 2008).
- Hydrogen can accelerate oxidation which may enhance initial stage SCC initiation. Hydrogen entered into the metal can decrease the stability of passive films and consequently can degrade the SCC resistance of alloys.
In nuclear power plant, the operational management level of DH is 25-35 cc STP/kg-H\textsubscript{2}O.

Japan plans to decrease the DH to a very low level, <5 cc/kg.

Recently, EPRI report that hydrogen increase to 60 cc/kg is sufficient to provide desired benefit to target components. Operation at lower hydrogen to achieve comparable benefit is not operationally practical.

In Europe, also consider to increase DH in PWR primary water.

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Objectives

Hydrogen has a strong effect on the corrosion behavior of alloys in the PWR primary water. However, the fundamental mechanisms of the effects of hydrogen on the corrosion and stress corrosion cracking are not well understood and a further investigation is needed.

- Investigated the effects of dissolved hydrogen on SCC initiation and small crack growth behavior.
- Help the optimization of DH in primary circuit water chemical composition.
- Comprehension of the effect of water chemical composition on SCC and oxidation.
2. Materials and experimental

Chemical composition of 316 stainless steel (from Sumitomo) wt%:

<table>
<thead>
<tr>
<th>elements</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05</td>
<td>0.37</td>
<td>1.46</td>
<td>0.026</td>
<td>0.001</td>
<td>11.52</td>
<td>16.58</td>
<td>2.08</td>
<td>0.052</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Machining process of the SSRT specimen:
Hollowed cylindrical specimen
Drilling and honing as per JIS standard.

drilled > honed
2. Materials and experimental- Test system

Test environments:
PWR primary water: 325 °C, 16 MPa, 500 ppm B (as H$_3$BO$_3$), 2 ppm Li (as LiOH)
DO<10 ppb. DH=5, 15, 30 and 50 cc/kg.
Slow strain rate tensile testing,
Strain rate: $\sim$2 x 10$^{-7}$ s$^{-1}$
SSRT test results

- The strain-stress curves show that the elongation of the specimen was affected by the DH significantly.
- The elongation of the specimen at 50 cc/kg is the highest, and that at 15 cc/kg is the lowest.
- The elongation of the honing specimen is larger than drilling specimen.
## SSRT test results

<table>
<thead>
<tr>
<th>DH (cc/kg)</th>
<th>Time</th>
<th>Strain at peak load (%)</th>
<th>Strain rate (s(^{-1}))</th>
<th>Maxium stress (MPa)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>316-drilled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>216h3m49s</td>
<td>16.825</td>
<td>2.163 × 10(^{-7})</td>
<td>386.73</td>
<td>rupture</td>
</tr>
<tr>
<td>15</td>
<td>185h30m3s</td>
<td>14.265</td>
<td>2.135 × 10(^{-7})</td>
<td>408.25</td>
<td>Not rupture</td>
</tr>
<tr>
<td>30</td>
<td>248h54m0s</td>
<td>18.035</td>
<td>2.013 × 10(^{-7})</td>
<td>418.89</td>
<td>Not rupture</td>
</tr>
<tr>
<td>50</td>
<td>215h9m38s</td>
<td>18.765</td>
<td>2.423 × 10(^{-7})</td>
<td>426.48</td>
<td>rupture</td>
</tr>
<tr>
<td>316-honed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>325h46m15s</td>
<td>25.015</td>
<td>2.194 × 10(^{-7})</td>
<td>435.03</td>
<td>rupture</td>
</tr>
<tr>
<td>15</td>
<td>284h41m06s</td>
<td>22.125</td>
<td>2.215 × 10(^{-7})</td>
<td>426.56</td>
<td>Not rupture</td>
</tr>
<tr>
<td>30</td>
<td>362h28m10s</td>
<td>29.525</td>
<td>2.322 × 10(^{-7})</td>
<td>459.07</td>
<td>Not rupture</td>
</tr>
<tr>
<td>50</td>
<td>386h31m28s</td>
<td>30.9</td>
<td>2.188 × 10(^{-7})</td>
<td>468.2</td>
<td>Not rupture</td>
</tr>
</tbody>
</table>
Crack morphologies: DH=5 cc/kg

The cracks in the honed specimen are shorter than those in the drilled specimen.
Crack morphologies: DH=15 cc/kg

Drilled specimen, DH=15 cc/kg

Honed specimen, DH=15 cc/kg

Cracks in the honed specimen are shorter than those in the drilled specimen.
Crack morphologies

- **Drilled specimen, DH=5 cc/kg**
- **Honed specimen, DH=5 cc/kg**

- **Intergranular cracking**

- **Drilled specimen, DH=50 cc/kg**
- **Honed specimen, DH=50 cc/kg**

- **Intergranular cracking**
Fracture surface morphology

- The fractographic morphologies for the drilled and honed specimens are similar, and there’s no obvious difference with various DH concentrations.
- Fractographic examinations show that some areas of transgranular (TG), mixed mode and cleavage fractures are seen on most fracture surfaces. Intergranular cracking is also observed in some areas.
- The cracks are transgranular at the initial site and then change to the intergranular feature.
Crack morphologies-long cracks

- All the long cracks are opened, some crack tips were filled with oxides, and some cracks have branches.
- The EDX-based chemical composition mapping reveals that the oxides in the crack and crack tips are Fe-Cr oxides.
Crack morphologies-short cracks

- The short cracks are closed
- The inner surface was covered by continuous oxide film, and some cracks are observed in the oxide film.
- It is believed that some of the cracks initiated from the damage of oxide film.
The number of the crack depth less than 5 μm is the largest.
Crack depth distribution-Honed specimen

316, 325 °C, PWR primary water, 500 ppm B, 2ppm Li, DH=5 cc/kg.
SSRT test, strain rate=2.194 x 10⁻⁷ s⁻¹

316, 325 °C, PWR primary water, 500 ppm B, 2ppm Li, DH=15 cc/kg.
SSRT test, strain rate=2.215 x 10⁻⁷ s⁻¹

316, 325 °C, PWR primary water, 500 ppm B, 2ppm Li, DH=50 cc/kg.
SSRT test, strain rate=2.423 x 10⁻⁷ s⁻¹

Observation gauge length
Average crack growth rate

Maximum crack growth rate

d_i is the depth of crack i, i is the crack number, t is the SSRT test time. a is the crack growth rate.

\[ a = \frac{\sum_{i=1}^{i=n} d_i}{nt} \]

n is the total number of cracks.

\[ a_{max} = \frac{d_{max}}{t} \]

\[ a_{max} \quad \text{honed < drilled} \]

Total crack number: honed < drilled
Effects of hydrogen
Crack open displacement of different crack depth

\[ \tan \alpha = \frac{\delta}{2d} \]

\[ \delta \] Crack open displacement

\[ d \] Crack depth

\[ 2\alpha \] Crack open angle

\[ \sum_{i=1}^{n} \tan \alpha_i \] Sum of crack open angles

\[ \frac{\text{Crack opening displacement}}{\text{Crack depth}} = \frac{\delta}{d} \]

COA = Crack open depth average

honed > drilled
Surface hardness: \( \text{drilled} > \text{honed} \)

Yield stress: \( \text{drilled} > \text{honed} \)

\[
\delta = \frac{\beta \sigma_0}{E} \ln \left( \frac{\lambda \varepsilon}{\sigma_0 d} \right)
\]

\( E \) is the Young’s module, \( J \) is the J-integral, \( \sigma_0 \) is the yield stress. \( \beta, \lambda, \varepsilon \) are constant.

COA: \( \text{drilled} < \text{honed} \)

\[ J.R. \, Rice, \, E.P. \, Sorensen, \, Journal \, of \, the \, Mechanics \, and \, Physics \, of \, Solids, \, 26 \, (1978) \, 163-186. \]
Discussion-effects of hydrogen and harden layer

A cross-section area weighted calculation of yield strength can be introduced to explain the effects of the hardened layer on the yield strength. \( \text{(from M.B. Toloczko)} \)

\[
\sigma_y(\text{average}) = \frac{\sigma_y(\text{base}) \times (A_{\text{hardened layer}} \times H_v_{\text{hardened layer}} + A_{\text{base}} \times H_v_{\text{base}})}{A_{\text{total}} \times H_v_{\text{base}}}
\]

\( \sigma_y(\text{average}) \) yield strength with a hardened layer.
\( \sigma_y(\text{base}) \) yield strength of unhardened material.
\( A_{\text{hardened layer}} \) cross sectional area of the hardened portion.
\( A_{\text{base}} \) cross sectional area of the unhardened portion.
\( H_v_{\text{hardened layer}} \) hardness of the hardened region.
\( H_v_{\text{base}} \) hardness of the unhardened portion.
\( A_{\text{total}} \) the total cross sectional area.

It could be calculated that the increased portion of \( \sigma_y \) by hardened layer are 2.99% for drilled specimen and about 0.55% for honed specimen respectively.

The yield strength of drilled specimen is about 20% higher than honed specimen.

Perhaps there were some effects due to hydrogen in the hardened layer, the yield stress could be increase significantly by the coupling interaction between hydrogen and hardened layer. \( \text{(International Journal of Hydrogen Energy, 39 (2014) 6095-6103.)} \)
Conclusions

- The SSRT test by use of hollowed cylindrical specimen with hardened inner surface by machining (Drilled and Honed) is a useful test for assessing the SCC susceptibility on non-sensitized stainless steels with the relatively short test time compared to a constant load test or crack propagation test.

- Drilled specimens showed enhanced SCC initiation and crack growth behavior compared to honed specimens but both showed a similar trend with the water chemistry with different DH levels. The propensity of crack initiation is greater in the drilled specimens because of much higher hardness in drilled specimen than the honed specimens.

- The fractographic morphologies for drilled and honed specimen are similar, and there is no obvious difference with various DH concentration. In both cases, cracks seem initiate initially transgranually and change to intergranular mode.

- The interaction of hydrogen and hardened layer play a important role on the crack initiation and crack growth.
Thank you very much for your attention