Stress Corrosion Cracking Behavior of Type 316L and Type 310S Stainless Steels in Fusion Relevant Environments

Yen-Jui Huang1 and Akihiko Kimura2

1Graduate School of Energy Science, Kyoto University, Uji 611-0011, Japan
2Institute of Advanced Energy, Kyoto University, Uji 611-0011, Japan

Stress corrosion cracking (SCC) susceptibility of type 316L and type 310S SS in pressurized water (561/613 K) and supercritical water (773 K) at deaerated condition and with dissolved-hydrogen (DH) ranging from 0.014 to 1.4 ppm were examined by means of slow strain rate test (SSRT) method at a strain rate of 5 × 10⁻⁶ s⁻¹. SCC susceptibility of type 316L SS depends on test temperature and DH content. The SCC susceptibility, which was evaluated as a brittle fracture ratio, increased with increasing test temperature from 561 to 613 K, while it became much smaller in supercritical water at 773 K. At 613 K, the fracture ratio of intergranular (IG) SCC increased with increasing DH content in the pressurized water, although almost no IGSCC was observed at 561 K at any DH conditions. However, the IGSCC initiated at near specimen surface and transferred to transgranular (TG) SCC inside the specimen. The SCC susceptibility of type 310S SS is significantly lower than that of type 316L SS in the hydrogenated water at 561 and 613 K, while the trend appears to be reverse at 773 K. It is suggested that higher DH content in water is necessary to trigger IGSCC than TGSCC at 613 K.

Keywords: SSRT, dissolved-hydrogen, pressurized water, supercritical water

1. Introduction

Type 316L stainless steel (SS) has been considered as one of candidate structural materials for fusion reactors.1-8 The steel will be mainly used in heat transfer system, delivering cooling water into plasma-facing components and bringing heat away. The system adopts double-loop design and operating condition of primary loop of ITER is similar to that of current pressurized light water reactors. Other proposals suggested using supercritical water as a coolant.9,10 In the fusion blankets, radiation-generated tritium may penetrate into cooling water. Tritium may react with water and form tritiated water and/or TH, T₂ tiny gaseous bubbles. Behaviors of these species resemble that of dissolved-hydrogen (DH) in water, which may enhance stress corrosion cracking (SCC) of type 316L SS and degrade the integrity of piping system of the blankets.

The effect of DH in cooling water has been investigated in past score. Hydrogen has been proved being able to harvest corrodants such as dissolved oxygen and hydrogen peroxides11 and consequently retarding crack growth rate (CGR).12,13 In pressurized water reactors, hydrogen is also responsible for controlling pH value. Since hydrogen concentration is critical for controlling cooling water, it should be kept within a certain value range while not degrading materials.13-15 Several studies reported that DH affected CGR on Ni-based alloys14-18 and stainless steels19-23 in simulated pressurized water environments.

Recently, we studied the SCC susceptibility of solution-annealed type 310S SS by means of slow strain rate test (SSRT) in hot water (561 K) with DH, and found that almost no SCC was observed in type 310S SS, while a remarkable SCC was found in type 316L SS showing a brittle fracture surfaces and cracks on specimen side surfaces.24 As for the effect of DH in the water on the SCC of type 316L SS, several researches were performed and the results varied among them. In the solution annealed steel, the minimum CGR was observed at 15 cc/kg at a temperature between 593 and 613 K, while in cold-worked type 316L SS, the maximum CGR was observed at 593 K.22 Fracture mode also varies among researchers, which might be due to test temperature difference: TGSCC at 561 K and IGSCC at 593 K. These above results indicates that SCC susceptibility depends on both temperature and DH in hot water.

Similar effects of hydrogen-assisted degradation can also be found in hydrogen gaseous environment. Han et al. tested susceptibility to hydrogen-induced cracking (HIC) of several austenitic steels in 1 MPa H₂ and D₂ gaseous environment. He reported that at around 200 K, type 310S SS was least susceptible, type 316 SS was next, and type 304 SS was most susceptible to HIC. Caskey also came up similar results from the tensile tests conducted in 69 MPa D₂ gas, indicating that the susceptibility decreased as Ni content increased between 15 to 25 mass%. Han, Chen and Lai attributed the susceptibility differences between austenitic SSs to the preference of martensite formation. Martensite allowed hydrogen to diffuse faster in materials, resulting in higher hydrogen concentration at crack-tip and accelerating crack growth. On the other hand, stabilized austenitic SS can prevent martensite formation hence reduces susceptibility to HIC. The relationship between HIC susceptibility and Ni content of steel was systematically examined by Zhang and his co-worker in a series of specially alloyed type 316L SS with different Ni equivalents. They tested these samples at temperatures ranging from 80 K to 300 K. Results revealed that the susceptibility decreased as Ni equivalent content increased from 24% to 33%.

Since hydrogen behavior in materials, such as diffusion, solubility and binding (trapping) behavior as well as corrosion reactions, is remarkably affected by temperature, it is considered that the SCC in hydrogenated water strongly depends on temperature and probably amount of hydrogen. Especially for application to fusion DEMO reactor, the temperature range of water is expected to be above 573 K and
possibly in supercritical water. In this work, we investigated the effects of temperature above 561 K and DH up to 1.4 ppm on the SCC of type 316L SS, which is a candidate structural material for coolant pipes of fusion reactors, and the SCC susceptibility of the type 316L SS will be compared with that of type 310S SS which is well known to be highly resistant to HIC.

2. Experimental

2.1 Testing materials

The materials used in this study are commercial rod shaped type 316L SS and type 310S SS provided by Nilaco Co. The chemical compositions are listed in Table 1. Remarkable difference in the chemical compositions between two steels are Cr, Ni and Mo. The steel rods were machined into round-bar type tensile specimens of which the geometries are shown in Fig. 1. The gage section of the specimen was 10 mm long and 2 mm in diameter. The specimen was screwed into the connection parts of the tensile machine. Prior the test, specimens were solution-annealed at 1323 K for 1 hour, followed by quenching into iced water. Specimen surfaces were polished by SiC sand papers from #800 to #4000 then cleansed in an ultrasonic cleaner.

2.2 Slow-strain rate test (SSRT)

Figure 2 is the schematic view of testing loop, which consists of a primary loop and a water chemistry monitoring loop. The primary loop was capable of providing pressurized water environment (15.5 MPa, 561–613 K) and supercritical water (25 MPa, 773 K) environment by manipulating a pressure relief valve. A high pressure pump drove water into a pre-heater, two autoclaves, heat-exchanger, and ion-exchanger and back to a water tank. A condenser dumped residual heat to an external chiller. High purity hydrogen and nitrogen were injected into the water tank to control dissolved-oxygen and DH. Deaerated water condition (both the dissolved oxygen and hydrogen are lower than 10 ppb) and the other three DH contents (0.014 ppm, 0.4 ppm and 1.4 ppm) were chosen to simulate different operating conditions. Strain rate was set at $5 \times 10^{-7} \text{s}^{-1}$. After SSRT, fractured surface and side surface were examined by scanning electron microscope (SEM).

3. Results

3.1 Deformation behavior

The stress-strain curves of solution-annealed type 316L SS tested at 561 K in pressurized water at deaerated and various DH content conditions are shown in Fig. 3, indicating that there is no remarkable change among the curves obtained for each water condition, although the DH content is different. However, the fracture behavior is affected by DH content significantly, and the detailed discussion will be given latter after showing fractured surface observation results.

The stress-strain curves in pressurized water at 613 K and supercritical water at 773 K at deaerated and various DH content conditions are shown in Fig. 4. Solid line represents deaerated water condition; dot line the DH = 0.014 ppm; dash-dot-dot line the DH = 0.4 ppm and dash line the DH = 1.4 ppm. Mechanical properties such as ultimate tensile strength (UTS) and total elongation (TE) were
summarized in Table 2. Comparing the curves among three testing temperatures, no trend nor remarkable difference was found between hydrogen-free and DH = 1.4 ppm in 561 K and 773 K. On the contrary, a clear DH dependence existed in the tensile properties at 613 K. Both UTS and TE decreased as DH content increased from 0 to 1.4 ppm. The UTS reduced from 430 MPa to 390 MPa; and TE reduced from 44% to 35%.

Stress-strain curves of solution-annealed type 316L SS tested at 613 K pressurized water (black line) and 773 K supercritical water (blue line) at deaerated condition (solid line); and with DH (DH) = 0.014 ppm (dot line), 0.4 ppm (dash-dot-dot line) and 1.4 ppm (dash line). The stress strain curve of 316L SS tested in a vacuum at a strain rate of 1 × 10⁻⁶ s⁻¹ is also shown.

3.2 Fracture mode examination

Fractured surfaces and side surfaces near necking region of solution-annealed type 316L SS tested at 561, 613 and 773 K at deaerated and DH = 1.4 ppm water condition are shown in Fig. 6. In each column, photos in left hand side represented fractured surface and photos in right hand side represented the side surface near necking region. Irrespective of water condition, it is clearly shown that the fracture mode depends on test temperature: a brittle fracture was only observed in the peripheral of the fractured surfaces at 561 and 613 K, while almost complete ductile fracture mode was observed at 773 K. The observation of side surface cracks revealed that crack opening and propagation were more significant at 613 K. In order to clear the DH dependence of fracture mode, the fracture behavior was investigated for tested specimens in hydrogenated water with DH = 0.014 and 0.4 ppm, as shown in Fig. 7, indicating similar results with Fig. 6. The reduction in area (RA) and the percentage of TG and IG area were summarized in Table 2 and Fig. 11, where brittle fracture ratio (BFR) is defined as a summation of TG and IG area ratio. Although the stress-strain behavior of solution-annealed type 316L SS at 561 K is not significantly affected by DH condition, fracture mode varies among the specimens tested in the different conditions. It was recognized that the most of fractured mode was TGSCC with typical river patterns on the fractured surface in which the percentage of TGSCC ranged from 30% to 45%, although there was no systematic DH dependence of the brittle fracture mode. As shown in Fig. 4, however, the total elongation was decreased with increasing DH content in hot water at 613 K, in which the fracture mode changed from TGSCC to a mixed mode of IGSCC initiation with propagation in TGSCC mode. The fraction of IGSCC increased with increasing DH content, while the total brittle fracture ratio appeared to decrease a bit. Figure 8 shows SEM photos of IGSCC/TGSCC transition region on the fractured surface of solution-annealed type 316L SS tested at 613 K in pressurized water with (a) deaerated, (b) DH = 0.014 ppm, (c) DH = 0.4 ppm and (d) DH = 1.4 ppm condition. The distance from surface to
Table 2  Summary of mechanical properties: YS (Yield Stress), UTS (Ultimate Tensile Strength), TE (Total Elongation), RA (Reduction of Area), TG\% (Area of transgranular cracking to area of fractured surface), IG\% (Area of intergranular cracking to area of fractured surface) and BFR (Brittle fracture ratio, defined as summation of TG and IG) of solution-annealed type 316L and type 310S SS tested at pressurized water (561/613 K) and supercritical water (773 K) environment with different DH content. Deaerated water condition is denoted as DH = 0 ppm.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Material</th>
<th>DH (ppm)</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>TE (%)</th>
<th>RA%</th>
<th>TG%</th>
<th>IG%</th>
<th>BFR%</th>
</tr>
</thead>
<tbody>
<tr>
<td>561</td>
<td>316L</td>
<td>0</td>
<td>124</td>
<td>421</td>
<td>41.9</td>
<td>40.3</td>
<td>51.4</td>
<td>0.0</td>
<td>51.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.014</td>
<td>90</td>
<td>411</td>
<td>45.1</td>
<td>52.2</td>
<td>31.8</td>
<td>0.7</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>121</td>
<td>438</td>
<td>39.4</td>
<td>40.3</td>
<td>51.8</td>
<td>0.0</td>
<td>51.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4</td>
<td>122</td>
<td>470</td>
<td>42.9</td>
<td>36.7</td>
<td>35.4</td>
<td>0.0</td>
<td>35.4</td>
</tr>
<tr>
<td>613</td>
<td>316L</td>
<td>0</td>
<td>101</td>
<td>433</td>
<td>44.4</td>
<td>37.3</td>
<td>25.3</td>
<td>0.0</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.014</td>
<td>104</td>
<td>431</td>
<td>42.2</td>
<td>41.7</td>
<td>39.5</td>
<td>6.8</td>
<td>46.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>122</td>
<td>390</td>
<td>34.2</td>
<td>31.8</td>
<td>22.0</td>
<td>17.3</td>
<td>39.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4</td>
<td>125</td>
<td>393</td>
<td>35.0</td>
<td>38.2</td>
<td>9.4</td>
<td>26.3</td>
<td>35.8</td>
</tr>
<tr>
<td>773</td>
<td>310S</td>
<td>0</td>
<td>147</td>
<td>486</td>
<td>53.6</td>
<td>63.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4</td>
<td>136</td>
<td>471</td>
<td>49.2</td>
<td>52.1</td>
<td>16.5</td>
<td>0.0</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>316L</td>
<td>0</td>
<td>88</td>
<td>444</td>
<td>48.5</td>
<td>57.6</td>
<td>6.0</td>
<td>0.0</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4</td>
<td>161</td>
<td>465</td>
<td>40.2</td>
<td>63.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>310S</td>
<td>0</td>
<td>143</td>
<td>478</td>
<td>53.1</td>
<td>57.8</td>
<td>15.3</td>
<td>0.0</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4</td>
<td>137</td>
<td>470</td>
<td>50.7</td>
<td>59.1</td>
<td>4.4</td>
<td>0.0</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Fig. 6  SEM photos of solution-annealed type 316L SS tested in pressurized water at (a) (b) 561 K, (c) (d) 613 K and in supercritical water at (e) (f) 773 K with (a) (c) (e) deaerated condition and with (b) (d) (f) DH = 1.4 ppm. In each column, photo in right hand side is side surface near necking region; in left hand side is fractured surface.
IG/TG intersection increases as DH content increases, indicating that IGSCC is enhanced by increasing DH at this temperature. At 773 K, however, fracture behavior was not affected by DH, as shown in Fig. 6 and 9.

As for type 310S SS, the SCC susceptibility in hydrogenated water is much lower than type 316L SS at 561/613 K, as clearly shown in Fig. 11 and Table 2. The TG area ratio of specimens tested at 561/613 K with DH = 1.4 ppm water condition appears to be higher than that with deaerated water condition. It is in agreement with the small reduction of TE. However, at 773 K, the TG area ratio of 310S SS appears to be larger than 316L SS, which is reverse trend of those at 561/613 K.

4. Discussion

4.1 SCC susceptibility at different temperatures

The above experimental results on type 316L SS showed that the SCC susceptibility rather depended on both test temperature and DH content. In this study, the highest SCC susceptibility was observed at 613 K which is the targeted coolant temperature of current design of fusion DEMO reactors. The most noticeable behavior is the change in the fracture mode from TGSCC to IGSCC with increasing test temperature from 561 to 613 K and DH content from almost zero (deaerated) to DH = 1.4 ppm. At 561 K, almost no IGSCC was observed on the fractured surface, although a very limited IGSCC initiation was recognized.22) Many previous researchers pointed out the contribution of hydrogen to the enhancement of SCC of solution annealed stainless steels in hydrogenated water as mentioned in the introduction.

The anodic-cathodic reaction at crack tip plays a critical role in crack progress. Anodic reaction involves metal dissolution while cathodic reaction involves water reduction. As temperature increases, the reaction rate increases and more hydrogen will be produced at near the crack tip. Meanwhile, hydrogen diffusivity increases and hydrogen binding reduces with increasing temperature. The alteration of fracture mode from TGSCC to IGSCC with increasing temperature from 561 to 613 K can be interpreted in terms of hydrogen trapping efficiency. TGSCC and IGSCC require each critical hydrogen content at dislocation and grain boundary, respectively. At 613 K, the hydrogen trapped at dislocations is much lower than at grain boundaries, since the binding energy of hydrogen with dislocation (20.2 kJ/mol) is almost one third of that with grain boundary (58.6 kJ/mol).23) Since hydrogen assisted intergranular cracking demands an enough amount of hydrogen at grain boundaries, we consider that the maximum amount of hydrogen is achieved at grain boundaries at around 613 K balancing the enhancement of
anodic reaction and reduction of hydrogen trapping efficiency. At 773 K, the trapping efficiency further decreases and hydrogen diffusivity increases, which leads to insufficient amount of hydrogen to induce IG and TGSCC, consequently brittle fracture ratio drastically reduces.

This test temperature dependence has been also observed for HIC of the steel, in which a critical amount of hydrogen is necessary to cause HIC, although the peak temperature is below room temperature in the case of HIC. This temperature dependence was interpreted in terms of hydrogen diffusion and trapping as follows. With increasing temperature the diffusivity of hydrogen becomes large but hydrogen trapping efficiency becomes small, consequently showing a peak temperature to maximize the amount of hydrogen at a trapping site. The increase in the ratio of IGSCC with increasing DH indicates the IGSCC requires more hydrogen than TGSCC. Figure 10 shows an IG fractured grains close to the specimen side surface of type 316L SS tested at 613 K at DH = 1.4 ppm water condition.

The total crack length per unit area on specimen surfaces near fractured region of all tested specimens was measured and depicted in Fig. 11; where circles represent SUS316L and triangles represent SUS310S. Since the crack length was measured on the specimen side surface, the susceptibility is might be correlated with crack nucleation behavior. Total crack length shows peaks at 613 K irrespective of material and DH, indicating highest crack nucleation at 613 K. It is noted that crack nucleation appears to be faster at 773 K than 563 K. Since the fracture mode observation revealed that SCC fracture ratio was larger at 563 K than 773 K, crack propagation could be faster at 561 K. The effect of amount of DH can be seen at 561 K where a higher DH caused a longer crack length suggesting hydrogen enhanced crack nucleation at 561 K, while the effect is not significant at 613 and 773 K. As for the difference between two steels, a marked suppression of SCC was recognized in SUS310 at 561 K.
The lower SCC susceptibility in type 310S SS at 561 to 613 K. At 773 K, the susceptibility of type 310S SS appeared of type 310S SS were smaller than type 316L SS at 561 and type 310S SS were larger than that of type 316L SS; and BFR than type 316L SS at 561 and 613 K. That is, RA and TE of SS is much more resistant to the SCC in hydrogenated water.

### 4.2 Comparison between 316L and 310S SS

Figure 12 clearly shows that solution-annealed type 310S SS in pressurized and supercritical water with deaerated and various dissolve-hydrogen water condition. Deaerated water condition is denoted as “DH = 0.” Black color represents intergranular (IG) crack, gray color represents transgranular (TG) crack and slash bar represents quasi-cleavage TG (QTG). Almost ductile behavior was found on following test conditions: type 316L SS in 773 K, DH = 1.4 ppm and type 310S SS in 561 K/613 K, DH = 0.

**Fig. 11** Total crack length per unit area on specimen surface near fractured region; where circles represent SUS316L and triangles represent SUS310S. Solid symbols are for deaerated water condition, open symbols for DH = 1.4 ppm.

**Fig. 12** Bar chart of brittle fracture ratio (BFR) of solution-annealed type 316L and type 310S SS tested in pressurized and supercritical water at deaerated and various dissolve-hydrogen water condition. Deaerated water condition is denoted as “DH = 0.” Black color represents intergranular (IG) crack, gray color represents transgranular (TG) crack and slash bar represents quasi-cleavage TG (QTG). Almost ductile behavior was found on following test conditions: type 316L SS in 773 K, DH = 1.4 ppm and type 310S SS in 561 K/613 K, DH = 0.

### 5. Conclusions

The susceptibility to SCC of solution-annealed type 316L SS and type 310S SS in pressurized water (561/613 K) and supercritical water (773 K) at deaerated condition and with DH ranging from 0.014 to 1.4 ppm were examined by means of SSRT at a strain rate of $5 \times 10^{-7}$ s$^{-1}$. The obtained main results are as follows:

1. SCC susceptibility of type 316L SS depends on test temperature and DH content. The SCC susceptibility a bit increased with increasing test temperature from 561 to 613 K, while it became much smaller in supercritical water at 773 K.

2. At 613 K, the fracture ratio of IGSCC increased with increasing DH content in the pressurized water, although almost no IGSCC was observed at 561 K at any DH conditions. The IGSCC initiated at very near specimen surface and transferred to TGSCC inside the specimen.

3. The SCC susceptibility of type 310S SS is significantly lower than that of type 316L SS in the hydrogenated water at 561 and 613 K, while the trend appears to be reverse at 773 K.

4. It is suggested that the DH content on specimen surface affects cracking behavior. Higher DH content was needed to trigger IGSCC at 613 K.

### REFERENCES


