Environmentally Assisted Cracking of Sensitized Stainless Steel in Supercritical Water: Effects of Physical Property of Water

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Cracking susceptibility of a sensitized 316 stainless steel has been evaluated in sub-critical and supercritical pure water as a function of applied pressure by using a slow strain rate test (SSRT). Effects of phase state of water and applied pressure, more essentially, physical property of water, were clearly observed. Although the sensitized 316 stainless steel was immune to stress corrosion cracking (SCC) in oxygenated “gas-like” supercritical water at 400°C/25MPa, cracking occurred at 400°C/30MPa and the cracking severity was more pronounced as applied pressure was increased up to 60MPa at the same temperature. This variation in cracking susceptibility being dependent on pressure was understood from “physical properties of water” point of view.

KEYWORDS: stress corrosion cracking, stainless steel, supercritical water, sub-critical water, physical property of water, dielectric constant, pressure effect, sensitization, slip dissolution mechanism

I. Introduction

The fourth state of water, supercritical water, holds great potential of industrial applications as a reaction medium for chemical industries and also as a coolant for energy conversion industries. One of the most difficult challenges to put the supercritical water processes to practical use is mitigation of environmentally assisted cracking of containment materials.

Physical properties of water, such as dielectric constant and ionic product, significantly vary with the density of water. In the supercritical conditions, since density of water widely varies with pressure, pressure has a strong influence on physical properties of water, as shown in Fig.1. Dielectric constant represents a character of water as a solvent and is one of the key parameters, which determine solubility of an inorganic compound including metal oxides. Dissociation equilibrium of an acid is also strongly dependent on water density. Dissociation constant of acid rises with increased density of water, resulting in drop of pH. Density of water and the density-related physical properties of water, therefore, are the major governing factors of corrosion of metals in supercritical aqueous solutions. It was demonstrated in literature that “physical property of water” point of view is indispensable to understand corrosion phenomena of metals in supercritical water. The water density is expected to have significant effects also on stress corrosion cracking (SCC) of metals in supercritical water. In this paper, we have looked into cracking behavior of a sensitized stainless steel in water under various pressures and at fixed temperature above and below the critical point, and discussed its correlation with dielectric constant of water.

II. Experimental Details

1. Material

An austenitic 316 stainless steel was used. The chemical composition is shown in Table 1. The material was solution treated (1050°C/30min, water cooled) and sensitized at 650°C for 24h. The degree of sensitization was evaluated by the Electrochemical Potentio-kinetic Reactivation Method and reactivation ratio of the material was 15.4%, which indicates well sensitized. Round bar type specimens, which have gauge section of 3mm in diameter and 20mm in length, were used.

Table 1 Chemical compositions of 316 stainless steel used .

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt%)</td>
<td>Bal.</td>
<td>17.46</td>
<td>12.35</td>
<td>0.03</td>
<td>0.58</td>
<td>0.82</td>
<td>0.032</td>
<td>0.002</td>
<td>2.07</td>
</tr>
</tbody>
</table>

![Fig.1 Phase diagram of water and dependence of physical properties of water on temperature and pressure.](image-url)
2. Cracking Experiments

The slow strain rate test (SSRT) was adopted to evaluate SCC susceptibilities of the material in sub-critical and supercritical pure water. The specimens were uniaxially pulled at a constant strain rate of 2.78×10^{-6}s^{-1}. The testing environment was distilled and then deionized water with 8ppm dissolved oxygen. Testing temperature/pressure combinations were 400°C/25MPa, 400°C/30MPa, 400°C/40MPa, 400°C/60MPa, and 360°C/25MPa. Phase state and dielectric constant of water are summarized in Table 2 for the testing conditions. This set of testing conditions covers wide range of dielectric constant, from 2.4 to 13.3.

Table 2 Testing temperature/pressure and phase state and dielectric constant of water.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Pressure</th>
<th>Phase of water</th>
<th>Dielectric constant</th>
<th>Oxygen concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C</td>
<td>25MPa</td>
<td>Supercritical</td>
<td>2.4</td>
<td>8ppm</td>
</tr>
<tr>
<td>400°C</td>
<td>30MPa</td>
<td>Supercritical</td>
<td>5.9</td>
<td>8ppm</td>
</tr>
<tr>
<td>400°C</td>
<td>40MPa</td>
<td>Supercritical</td>
<td>10.5</td>
<td>8ppm</td>
</tr>
<tr>
<td>400°C</td>
<td>60MPa</td>
<td>Supercritical</td>
<td>13.3</td>
<td>8ppm</td>
</tr>
<tr>
<td>360°C</td>
<td>25MPa</td>
<td>Liquid</td>
<td>13.4</td>
<td>8ppm</td>
</tr>
</tbody>
</table>

III. Results and Discussions

Stress-strain curves obtained in the SSRTs are shown in Fig.2. In the sub-critical water at 360°C/25MPa, the specimen failed in intergranular mode with failure strain of about 12%. This result indicated high susceptibility of the sensitized stainless steel to SCC in the oxygenated sub-critical water. It is well recognized from extensive reseraches\textsuperscript{5}) on BWR components that sensitized stainless steels are highly susceptible to intergranular stress corrosion cracking (IGSCC) in a high-temperature water, which contains a few ten ppb or higher level of oxygen. The SSRT result in the sub-critical condition is consistent with the previous BWR studies. As for supercritical conditions, cracking susceptibility was strongly affected by the applied pressure. Although the specimen failed in ductile mode with elongation of about 45% and no crack was found in the "gas-like" condition at 400°C/25MPa, failure strain monotonically decreased as the pressure was increased. Failure strain reduced down to about 21% when the pressure was increased to 60MPa. Fracture surfaces of the specimens are shown in Fig.3. Failure mode was almost fully intergranular for the sub-critical condition. Failure morphology varied with applied pressure at 400°C. Although only transgranular cracks were found under relatively low pressure, e.g. 30MPa, where reduction in failure strain was not significant, intergranular fracture appeared under higher pressure conditions. The failure strain, which represents SCC susceptibility, is plotted as a function of dielectric constant of water for the testing conditions, Fig.4. These results indicate that cracking is more enhanced under higher dielectric constant condition, including both sub-critical and supercritical water.

In a medium having high dielectric constant, ionization of metal is easier and solubility of metal oxide is higher. In addition, electric conductivity of water is higher for higher dense condition, since ionic product is higher. Hence, anodic dissolution of metal in water is more enhanced under a high-dielectric constant condition. The result shown in Fig.4, therefore, clearly indicates that dissolution of metal holds

Fig.2 Stress-strain curves of sensitized 316SS in supercritical and sub-critical pure water at strain rate of 2.78x10^{-6}s^{-1}. Both maximum stress and failure strain were remarkably reduced as pressure was increased at 400°C.
the essential role in the cracking phenomena of a sensitized stainless steel in supercritical and sub-critical pure water. The slip-dissolution mechanism, which is one of the dissolution-driven cracking mechanisms, was proposed for sensitized stainless steels in the BWR coolant environment and widely accepted. Direct experimental evidence, however, have not been sufficient. The results of this study would provide a strong evidence of the dissolution mechanism.

Cracking susceptibility seems somewhat higher for sub-critical 360°C/25MPa condition compared with supercritical 400°C/60MPa condition, although dielectric constant is almost the same for the both conditions. From a crevice chemistry point of view, difference in diffusivity of ionic species between supercritical water and sub-critical water might have some effect. Direct effect of temperature on kinetics would also be there.

IV. Conclusion

Cracking susceptibility of a sensitized 316 stainless steel has been evaluated in sub-critical and supercritical pure water as a function of applied pressure by using a slow strain rate test (SSRT). Conclusions may be drawn as follows;

(1) Effects of phase state of water and applied pressure, more essentially, physical property of water, were clearly observed.
(2) SCC did not occur in the oxygenated “gas-like” supercritical water at 400°C/25MPa.
(3) Cracking occurred at 400°C/30MPa and the cracking severity was more pronounced as applied pressure was increased up to 60MPa at the same temperature.
(4) This variation in cracking susceptibility being dependent on pressure was understood from dielectric

![Fracture morphologies of SSRT specimens.](image)

**Fig.3** Fracture morphologies of SSRT specimens.

![Graph](image)

**Fig.4** Failure strain in SSRT plotted as a function of dielectric constant of water
constant of water.
(5) The results give a strong evidence of the dissolution mechanism.

Acknowledgment
Part of the work was supported by the Grant-in-Aid for Scientific Research (B) (No.13450290) and for COE Research (No.11CE2003), The Ministry of Education, Sports, Culture, Science and Technology.

References