OXIDATION BEHAVIOR AND CRACKING SUSCEPTIBILITY OF Ni-Cr ALLOYS IN DRY STEAM AND INERT GAS UNDER EXTREMELY-LOW OXYGEN PARTIAL PRESSURE

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1. Introduction
Stress corrosion cracking (SCC) of structural alloys in a light-water reactor is one of the most considerable issues for the safe plant management. Since SCC thought to be a complex phenomenon which relates material, environment and mechanics factors, the mechanism of SCC is not fully understood. In the recent findings, the internal oxidation with selective oxidation of specific alloying elements was observed near the crack tip of L-grade stainless steels in boiling water reactor (BWR) environment and of Ni-base alloys in pressurized water reactor (PWR) primary water environment by using analytical transmission electron microscope (ATEM) [1]. Furthermore, selective internal oxidation (SIO) is proposed as a mechanism of intergranular stress corrosion cracking (IGSCC) of Ni-base alloys in high temperature water [2].

In this study, assuming that solid state-oxidation is fundamental mechanism of IGSCC, oxidation behavior and cracking susceptibility of Ni-Cr alloys with different Cr content under extremely-low oxygen partial pressure have been investigated by oxidation experiments using plate specimens and Reverse U-Bend (RUB) specimens for 750 hours at 400 °C in two kinds of gas system (inert gas and dry steam) under various oxygen potential range (Ni stable, Ni/NiO equilibrium and NiO stable).

2. Experimental
2.1 Materials
Three kinds of Ni-Cr alloys with different Cr content (Ni-14Cr, Ni-22Cr, and Ni-30Cr) were made for this study. The alloys were solution heat-treated at 1180 °C for 30 minutes after homogenizing heat-treatment at 1230 °C for 10 hours and hot-rolling. Chemical compositions of the alloys were shown in Table 1. Plate specimens and RUB specimens were made from the alloys, and used for the oxidation experiments.

<table>
<thead>
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<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>O</th>
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<td>Ni-14Cr</td>
<td>Bal.</td>
<td>13.89</td>
<td>0.014</td>
<td>0.049</td>
<td>0.008</td>
<td>&lt;0.001</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>0.006</td>
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<tr>
<td>Ni-22Cr</td>
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<td>0.019</td>
<td>0.046</td>
<td>0.003</td>
<td>0.007</td>
<td>0.001</td>
<td>&lt;0.001</td>
<td>0.004</td>
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<tr>
<td>Ni-30Cr</td>
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<td>0.029</td>
<td>0.044</td>
<td>0.002</td>
<td>0.012</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.003</td>
</tr>
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</table>

2.2 Oxidation Experiments
Oxidation experiments were performed in two kinds of gas system, one is ”inert gas system”, which consist of inert gas and trace oxygen, and the other is ”dry steam system (hydrogenated superheated steam)”, under various oxygen potentials. The reason that the gas systems were
adopted for environment of the experiments is to evaluate “water molecule effect” on characteristics of oxide and cracking susceptibility of Ni-Cr alloys. The target $P_{O_2}$ of the experiments was determined based on alloying elements (Ni, Cr)/oxide equilibrium. Since it is possible that the actual $P_{O_2}$ might be different from the target $P_{O_2}$, pure metal (Cu, Fe, Ni, and Co) specimens were also set in the test section to monitor the actual $P_{O_2}$ range. Fig.1 shows target $P_{O_2}$ and actual $P_{O_2}$ ranges in the experiments, and suggests that the actual $P_{O_2}$ is lower than target $P_{O_2}$ in all the experiments.

3. Result and Discussion

3.1 Inert gas system (with trace $O_2$, without $H_2O$)

The surface oxide and cracking morphologies of RUB specimen in NiO stable condition ($logP_{O_2}= -19 \sim -15$) are shown in Fig.2. Cracks have been observed in all the specimens, and surface morphology and cracking susceptibility seems to be totally different between the Ni-14Cr and the others. The ragged surface morphology and a number of millimeter-scale IG cracks have been observed in the Ni-14Cr; on the other hand, relatively smooth surface morphology and only one small crack have been observed in the Ni-22Cr and Ni-30Cr, respectively. The difference in cracking susceptibility is considered to be caused by protective oxide film formed or not. It has been also suggested that the threshold level of Cr content required for the protective oxide film to form in the $P_{O_2}$ range locates somewhere in between 14 wt% and 22 wt%. However, even Ni-30Cr was not immune to IG cracking in the NiO stable condition.

Fig.3 shows TEM micrographs and EDS mapping at crack tip of Ni-14Cr. The result of TEM analysis indicated no grain boundary oxidation ahead the crack tip, and Cr depletion along the grain boundary ahead the crack tip as long as ~3μm.
The surface morphology of RUB specimen in Ni stable condition (log$P_{O_2} = -35 \sim -29$) are shown in Fig.4. No crack has been found in all Ni-Cr alloys, but the surface morphology of Ni-22Cr seems more ragged compared with that of the others.

3.2 Dry steam system (hydrogenated superheated steam)

The surface oxide and cracking morphologies of RUB specimen in near Ni/NiO equilibrium (log$P_{O_2} = -29 \sim -28$) are shown in Fig.5. Cracks have been observed in all the specimens tested near Ni/NiO equilibrium, and cracking severity was highest for Ni-14Cr and lowest for Ni-30Cr same as in the case in NiO stable condition- inert gas system. Fig.6 shows the surface morphology of RUB specimen in near NiO stable condition (log$P_{O_2} = -25 \sim -19$). Smooth surface and no crack were found in all the specimens at NiO stable condition.

3.3 Summary of cracking susceptibility

The cracking susceptibility in all the experiments has been summarized in Table2. It has been suggested that potential range for the cracking susceptibility seemed to be different between the two environments; near Ni/NiO equilibrium in hydrogenated steam, while higher $P_{O_2}$ for the inert gas system. Further characterizations focused on the oxide film characteristics are needed to reveal the reason for the cracking susceptibility in the certain potential range described above.

Fig. 2 NiO stable-inert gas: appearance and cross-sectional view of RUB specimen

Fig. 3 NiO stable-inert gas: TEM micrographs and EDS mapping at crack tip of Ni-14Cr
4. Summary
1) The Ni-Cr alloys cracked along grain boundary both in inert gas system (with trace O$_2$, without H$_2$O) and in hydrogenated steam.
2) Potential range for the cracking susceptibility seemed to be different between the two environments; near Ni/NiO equilibrium in hydrogenated steam, while higher P$_{O2}$ for the inert gas system.
3) Cracking severity was highest for Ni-14Cr and lowest for Ni-30Cr both in inert gas and steam. But even Ni-30Cr was not immune to IG cracking in steam near Ni/NiO equilibrium.

References