Stress Corrosion Cracking Behavior of Zirconium in Boiling Nitric Acid Solutions at Oxide Formation Potentials

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Zirconium has been utilized in nuclear fuel reprocessing plants because of its superior corrosion resistance in nitric acid solutions. However, stress corrosion cracking (SCC) susceptibility of zirconium has been reported in boiling nitric acid solutions at the passivity breakdown potential. However, it has not been clear the SCC initiation and propagation behavior of zirconium.

In this study, to clarify the SCC initiation and propagation behavior of zirconium, constant load tensile tests were carried out in boiling nitric acid solutions.

From the results, many cracks were initiated under the oxide film and maximum crack led to rupture in the potentials that nobler than passivity breakdown potential. These results showed that the SCC of zirconium in boiling nitric acid solutions is due to the oxide formation. And this SCC behavior suggests that the SCC behavior of zirconium can be attributed to tarnish rupture model.

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1. Introduction

The nuclear fuel cycle is an important system for maintaining a stable energy supply in Japan. Nuclear reprocessing plants play an important role in the nuclear fuel cycle. However, marginal research and development efforts focused on nuclear fuel reprocessing technology are being carried out.

In Japan, a nuclear reprocessing plant has been operating at Tokai, and a pilot-scale operation has been investigated to determine the potential for a commercial-scale operation at the Rokkasyo reprocessing plant. The PUREX process using nitric acid and dodecane with tributyl phosphate as the solvent has been adopted in these plants.

Hence, the equipment in nuclear fuel reprocessing plants is exposed to a severe corrosive environment such as concentrated boiling nitric acid solutions. Therefore, structural materials used in nuclear fuel reprocessing plants require superior corrosion resistance in boiling nitric acid solutions.

It is known that zirconium has superior corrosion resistance in nitric acid solutions.1–3) Based on these reports, the International Atomic Energy Agency (IAEA) concluded in a technical document (IAEA TECDOC-421) that zirconium is an excellent material for use in a nitric acid environment because of its superior corrosion resistance.4) The corrosion resistance of zirconium in a simulated spent nuclear fuel solution was also evaluated in some reports.5,6) They concluded that zirconium has superior corrosion resistance in boiling nitric acid solutions containing Pu.

However, some studies observed that zirconium is susceptible to stress corrosion cracking (SCC) in nitric acid. Kajimura et al. evaluated SCC susceptibility using a slow strain rate test (SSRT) in a boiling nitric acid solution. They observed that the nitric acid solution concentration and corrosion potential for SCC have an effect on the susceptibility of zirconium to SCC in a boiling nitric acid solution.7) Bernard et al. studied the corrosion and SCC properties of zirconium used in the La Hague nuclear fuel reprocessing plant in France and reported that zirconium is susceptible to SCC, as indicated by a remarkable ductility loss, at the passivation breakdown potential.8) Thus, the IAEA technical document (IAEA TECDOC-421) concluded that zirconium is susceptible to SCC in nitric acid solutions with a concentration greater than 65 mass%.

However, these reports discussed only the SCC susceptibility using the SSRT to evaluate reduction of the elongation and besides the SCC crack generation behavior to understand the SCC mechanism of zirconium in a boiling nitric acid solution did not discuss. And Kato et al. reported that Zr showed creep deformation under elastic stress in boiling nitric acid solution.9) This report suggests that it is difficult to divide the deformation value among SCC and creep from time-displacement curve in tensile test. Therefore, it is important to evaluate the crack initiation and progression behavior of SCC because they are useful to predict the SCC occurrence condition and the lifetime for nuclear fuel reprocessing plants.

In this study, the constant load tensile test method with control the applied potentials of zirconium in boiling nitric acid solutions was used to understand the initiation and progression mechanism of SCC.

2. Experimental Procedures

2.1 Test samples

An ASTM B551-85 R60702 grade pure zirconium rolled plate was used as the test material. Table 1 shows the chemical composition of the material along with the composition specified in the ASTM R60702 standard. Rod-shaped specimens (φ3 × 20 mm gauge) were used for the constant load tensile tests. Figure 1 shows a schematic view of a constant load tensile test specimen.
and the boiling point of these solutions was approximately 387 K. The constant load test was stopped at $1.80 \times 10^6$ s owing to time restrictions. If the specimens did not rupture within $1.80 \times 10^6$ s, the specimens were presumed as “Not rupture”. To observe the time dependency of SCC crack growth, constant load tests (9 mol/L boiling nitric acid solution, 1.4 V vs. SSE) were stopped at intermediate times ($8.64 \times 10^5$, $1.73 \times 10^5$, $3.46 \times 10^5$, $6.91 \times 10^5$, $8.89 \times 10^5$ and $1.32 \times 10^6$ s).

### 2.4 Analysis

The surface appearance was investigated to evaluate oxide film formation. The fracture surface was evaluated by secondary electron microscopy (SEM) analysis. A cross-sectional observation was performed to evaluate crack propagation by reflection electron microscopy.

### 3. Results and Discussion

Figure 3 shows the anodic polarization curve of zirconium in a 9 mol/L boiling nitric acid solution. The applied potential range of this test (from 1.0 to 1.5 V vs. SSE) is also shown in this figure.

Figure 4 shows the time-displacement curves for the constant tensile load test in that the applied potentials were from 1.0 to 1.45 V vs. SSE. These results indicated that the rupture time decreased as the applied potential increased.

Figure 5 shows the appearance of the specimens after the constant load tensile tests. Some specimens ruptured at the gauge without any ductile deformation, such as by cup and cone fractures. All specimens ruptured when they were covered with a thick film. The thick film was zirconium oxide by energy dispersive X-ray spectrometry. The black thick oxide film formation was observed when the applied potentials were nobler than passivity breakdown potential (around 1.40 V vs. SSE). However, specimens did not rupture when they were covered with a yellow or gold passive film. These results suggested that the thick oxide film induces SCC crack generation.

Figure 6 shows the relationship between the rupture time and the applied stress during the constant load tensile tests. The rupture time decreased with increasing applied stress. From Fig. 4, there was no difference in deformation behaviors between ruptured specimens and not-ruptured specimens until rupture. This result suggests that the deformation value caused by SCC was masked by creep deformation value. It is considered that crack propagation rate is very rapid when rupture. These results suggested that the incubation period of specimen failure decreases with applied stress increase.

Figure 7 shows the relationship between the rupture time and the applied potentials. From these results, it was observed that the rupture time rapidly decreased at threshold potentials. An increasing applied stress also led to a decrease in the rupture time, but the effect of the potential was more dominant than that of the applied stress. From these results, it was determined that the threshold potential is around 1.40 V. And according to Fig. 5, the threshold potential is same as the potentials associated with the generation of the thick oxide film. These results also suggest that the thick oxide film influences SCC susceptibility.

### Table 1  Chemical composition of the test material and ASTM R60702 specification (mass%).

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Fe + Cr</th>
<th>Hf</th>
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<td>Test material</td>
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<td>0.003</td>
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<td>&lt;0.01</td>
<td>&lt;0.003</td>
<td>0.16</td>
<td>0.2</td>
<td>4.5</td>
<td>bal.</td>
</tr>
</tbody>
</table>

![Schematic view of the constant load tensile test specimen (mm).](image1)

![Schematic view of the electrochemical cell.](image2)

2.2 Test apparatus

Figure 2 shows a tensile test machine with an electrochemical cell used for constant load tensile tests with controlled applied potentials. A nitric acid solution was heated to boil using a tin oxide transparent heater that coated the electrochemical cell. The corrosion potential was controlled by a potentiostat with a saturated KCl–Ag/AgCl reference electrode. A platinum electrode was used as the counter electrode. A glass tube with glass filter containing a 14.4 mol/L nitric acid solution was used as the liquid junction for the measurement of potentials in the boiling solutions. This junction was used to avoid interruption due to bubble formation inside the liquid junction. The correction of potentials was not carried out because the potential shift using this junction was less than approximately 10 mV.

2.3 Test conditions

To determine the applied potentials, an anodic polarization test for zirconium was carried out in a 9 mol/L boiling nitric acid solution. The stresses for the constant load test were chosen as 100, 150 and 200 MPa. Test stresses were in elastic deformation region. The solution concentration was 9 mol/L, and the boiling point of these solutions was approximately 387 K. The constant load test was stopped at $1.80 \times 10^6$ s owing to time restrictions. If the specimens did not rupture within $1.80 \times 10^6$ s, the specimens were presumed as “Not rupture”. To observe the time dependency of SCC crack growth, constant load tests (9 mol/L boiling nitric acid solution, 1.4 V vs. SSE) were stopped at intermediate times ($8.64 \times 10^5$, $1.73 \times 10^5$, $3.46 \times 10^5$, $6.91 \times 10^5$, $8.89 \times 10^5$ and $1.32 \times 10^6$ s).

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All the above results indicate that the thick oxide film plays an important role in SCC initiation and propagation. Therefore, the cross-sectional observations of the gauge were carried out after the constant load tensile test (boiling 9 mol/L nitric acid, 200 MPa, 1.4 V vs. SSE) was halted at intermediate times ($6.00 \times 10^2$, $8.64 \times 10^4$, $6.12 \times 10^5$ and $1.80 \times 10^6$ s).

Figures 8 to 11 show the reflection electron micrograph of the gauge cross section after $6.00 \times 10^2$, $8.64 \times 10^4$, $6.12 \times 10^5$ and $1.80 \times 10^6$ s (Fig. 8). These ball-like oxides become oxide film by growth and link. And many microcracks were observed under the oxide film after $8.64 \times 10^4$ s (Fig. 9). These microcracks were filled with oxide from the
composition image by reflection electron microscopy. After $6.12 \times 10^5$ s, few of these cracks were propagated about 20 µm (Fig. 10). And after $1.80 \times 10^6$ s, one of these cracks was propagated about 1000 µm (Fig. 11). These results confirm that SCC microcracks generate under the thick oxide film at the initial stages of the constant load tensile test in the oxide formation potential region. And the thick oxide film is brittle because crack is observed in oxide film.

Figure 12 shows that schematic view of SCC initiation and propagation behavior of Zr in boiling nitric acid solutions at oxide formation potential. The initiation and propagation behaviors are as follows: (i) brittle oxides generate on the surface of Zr (Fig. 8); (ii) microcracks initiated under the brittle oxide film (Fig. 9); (iii) some cracks propagate (Fig. 10); and (iv) one of the longest crack propagated until failure (Fig. 11).

From above results, we discuss about SCC mechanism of Zr in boiling nitric acid solution. Active Pass Corrosion (APC), Hydrogen Embrittlement (HE) and Tarnish Rupture (TR) are known as SCC mechanisms. Figure 13 shows...
current density of Zr during constant load tensile test (boiling 9 mol/L nitric acid, 200 MPa, 1.4 V vs. SSE). At first, current density increases with test time but current density decreases to microampere range after $10^4$ s. And from cross section observations (Figs. 8–11), the thick oxide film covers the surface of Zr. From these result, the thick oxide film that generate at a nobler potential than passivity breakdown potential has insolubility in boiling nitric acid solution. We consider that SCC mechanism of Zr in boiling nitric acid solution can be explained by TR. Because, TR occurs under constant tensile load conditions that generate thick tarnish films.10,11)

In TR, SCC initiates at the brittle tarnish film on the surface of metal owing to tensile stress. TR propagates as a result of the repetition of tarnish film generation and failure at the crack tip. Therefore, the TR fracture surface exhibits a step-like pattern. Figure 14 shows SEM micrograph of the fracture surface after constant load tensile test (1.4 V vs. SSE, 200 MPa). From this micrograph, step-like transgranular brittle pattern was observed at fracture surface.

4. Conclusions

The SCC initiation and propagation behavior of zirconium in boiling nitric acid solutions at transpassive potentials can be described as follows:

SCC occurs at and above the threshold corrosion potential where a black oxide film is generated.

SCC cracks are initiated under the oxide film that is generated on the zirconium surface.

A small number of longer cracks can propagate until failure.

The fracture surface exhibits a step-like transgranular brittle pattern.

Therefore, the SCC behavior of zirconium in a boiling nitric acid solution at transpassive potentials can be explained by the tarnish rupture mechanism.

REFERENCES