Corrosion Fatigue of Refractory Materials in Boiling Nitric Acid *

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Refractory materials such as zirconium, niobium and titanium alloys with excellent corrosion resistance in boiling nitric acid have been selected for use as structural materials of spent fuel reprocessing equipment. In this study, the fatigue crack growth rates of these materials were investigated by load control tests as a function of the stress intensity factor range in boiling 3 kmol/m3 nitric acid and in air at room temperature. The fracture surfaces were observed by scanning electron microscopy. The fatigue crack growth rates of zirconium and niobium were enhanced in boiling nitric acid compared with those in air at room temperature. Acceleration effect due to corrosion fatigue was not observed in the crack growth of Ti–5Ta alloy. The fracture surfaces of Ti–5Ta alloy showed the ductile striation in both environments. On the other hand, the fracture surfaces of niobium represented the fatigue striation in air and the brittle striation due to corrosion in nitric acid. The fracture surfaces of zirconium in nitric acid showed brittle fracture and the ductile fracture related to stress corrosion cracking.

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Keywords: corrosion fatigue, refractory metal, zirconium, titanium alloy, niobium, nitric acid, stress corrosion cracking, striation

1. Introduction

Stainless steels are subject to intergranular attack in nitric acid environments, whereas refractory metals such as zirconium, niobium and Ti–5Ta alloy have excellent corrosion resistance.1, 2) Ti–5Ta alloy and niobium have little susceptibility to stress corrosion cracking (SCC) in boiling nitric acid solution,3,4) however zirconium has the SCC susceptibility.4–11) Recently, zirconium and Ti–5Ta alloy have been applied to the equipment of nuclear spent fuel reprocessing plants,12, 13) where a large amount of nitric acid is used. And so the fatigue behavior should be evaluated for the reliability of spent fuel reprocessing plant components made of these materials by considering the cyclic stress due to the practical operation. Especially the effect of SCC on the fatigue behavior is considered to be an important issue.

In this viewpoint the fatigue crack growth rates of Ti–5Ta alloy, niobium and zirconium were investigated in boiling 3 kmol/m3 nitric acid and in air at room temperature as a reference. The fatigue crack growth rate was obtained as a function of the stress intensity factor range. In addition, the fatigue crack growth mechanism was analyzed by fractography, X-ray diffraction method and corrosion tests.

2. Experimental Procedures

2.1 Materials and specimen geometry

The tested materials were three plates made of pure zirconium, pure niobium and Ti–5Ta alloy with the commercial grade composition as shown in Table 1. Ti–5Ta alloy contains 5.1 mass% tantalum. The grains of zirconium and Ti–5Ta alloy were of a size, ASTM No. 6.5, and the grain size of niobium was ASTM No. 2.5. The test specimens were tapered double cantilever beam (TDCB) type as shown in Fig. 1. They were cut out of the plates. The surface of each specimen was polished up to 1 μm diamond paste for optical observation of crack length. The specimen has the transverse orientation in plate;14) the loading direction is perpendicular to the rolling direction, thus crack propagation direction is parallel to the rolling direction. This orientation shows the high SCC susceptibility in the case of zirconium.5,8)

2.2 Environments

Nitric acid solution with 3 kmol/m3 was selected as a test solution. This concentration is the minimum value for showing the SCC susceptibility in zirconium10) and corresponds to the nitric acid concentration at a dissolver in reprocessing plants.13) The fatigue test was conducted at boiling point 378 K under free corrosion potential. The reference data on the same load control condition were obtained in air at room temperature.

2.3 Measurement of fatigue crack growth rates

The test specimen was set in a corrosion cell made of corrosion resistant materials.15) A closed-loop servo-hydraulic type fatigue machine was used in fatigue tests. The crack growth length from pre-crack to crack tip was monitored with an optical microscope during the tests. The crack length, a, was obtained in relation to the number of cycles, N, applied at a given load amplitude, ΔP. The load P was given a sinusoidal variation with a stress ratio of \( R = P_{\text{min}} / P_{\text{max}} = 0.1 \) and a

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Table 1 Chemical composition of materials used in the present study (mass%).

<table>
<thead>
<tr>
<th>Material</th>
<th>Ti</th>
<th>Ta</th>
<th>Fe</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–5Ta alloy</td>
<td>Bal.</td>
<td>5.1</td>
<td>0.020</td>
<td>—</td>
<td>0.0009</td>
<td>0.0031</td>
<td>0.08</td>
</tr>
<tr>
<td>Niobium</td>
<td>Nb</td>
<td>Ta</td>
<td>Fe</td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>O</td>
</tr>
<tr>
<td>Bal.</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>&lt;0.001</td>
<td>—</td>
<td>0.003</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Zirconium</td>
<td>Zr + Hf</td>
<td>Hf</td>
<td>Fe + Cr</td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>O</td>
</tr>
<tr>
<td>≥ 99.2</td>
<td>0.3</td>
<td>0.11</td>
<td>0.01</td>
<td>&lt;0.0005</td>
<td>0.008</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2 Crack growth rates of zirconium in boiling 3 kmol/m³ nitric acid and in air at room temperature.

Fig. 3 Crack growth rates of niobium in boiling 3 kmol/m³ nitric acid and in air at room temperature.

frequency of $f = 0.1$ Hz. The experiment started after the pre-fatigue cracking in air. A relationship of the fatigue crack growth rate, $da/dN$, as a function of the stress intensity factor range, $\Delta K$, was obtained from the above measurements.

2.4 Fracture surface analysis

After the measurement of fatigue crack growth rates, the fracture surface of test specimen was observed by a scanning electron microscope (SEM). The crystallographic orientation of fracture surface was analyzed by X-ray diffraction (XRD) method.

2.5 Corrosion tests

Anodic polarization curves of Ti–5Ta alloy, niobium and zirconium were measured in boiling 3 kmol/m³ nitric acid. The potential sweep rate was controlled in 0.333 mV/s. A reference electrode was an Ag/AgCl electrode and a counter electrode was a platinum plate. Immersion tests for 240 hours were also conducted in boiling 3 kmol/m³ nitric acid. The ratio of solution volume to surface area of specimen was about 80 mL/cm².

3. Results

3.1 Fatigue crack growth rates

As shown in Fig. 2, the fatigue crack growth rate of zirconium was accelerated in nitric acid solution due to corrosion fatigue compared with that in air. The acceleration factor was about four at $\Delta K = 8$ MPa m$^{1/2}$.

The fatigue crack growth rate of niobium was also enhanced in nitric acid solution as shown in Fig. 3. The acceleration factor was approximately four at $\Delta K = 12$ MPa m$^{1/2}$.

On the other hand, the fatigue crack growth rate of Ti–5Ta alloy was almost the same in nitric acid solution as in air (Fig. 4). The crack growth rate in high $\Delta K$ was slightly higher in nitric acid than in air.

3.2 Fractography

Figure 5(a) shows the fracture surface of zirconium tested in nitric acid showed the typical morphology expected in corrosion fatigue related to SCC. It is expectable as a pseudo-cleavage along a basal plane {0001} which is the cracking path of SCC and a fluting along prismatic plane {1010}.16 On the other hand, the fatigue striation due to the plastic deformation was observed in air as shown in Fig. 5(b). In both cases, the plastic deformation would be taken place by slip on the same crystal system along the prismatic plane. This is characterized in the fatigue crack growth behavior of zirconium.

Figure 6 shows the fracture morphology of Ti–5Ta alloy. The fatigue striation controlled with the plastic deformation was observed without any morphological difference between in air and in nitric acid.

The morphology of fracture surfaces in niobium was almost the same in both environments as seen in Fig. 7. However, the corrosion fatigue enhanced by the chemical dissolu-
Fig. 4 Crack growth rates of Ti–5Ta alloy in boiling 3 kmol/m³ nitric acid and in air at room temperature.

Fig. 5 SEM photographs of the fracture surface of zirconium tested in boiling 3 kmol/m³ nitric acid (a) and in air at room temperature (b).

Fig. 6 SEM photographs of the fracture surface of Ti–5Ta alloy tested in boiling 3 kmol/m³ nitric acid (a) and in air at room temperature (b).

Table 2 Corrosion rates of tested materials evaluated by weight loss in boiling 3 kmol/m³ nitric acid.

<table>
<thead>
<tr>
<th>Material</th>
<th>Corrosion rate (mm/y)</th>
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<tr>
<td>Ti–5Ta alloy</td>
<td>0.0160</td>
</tr>
<tr>
<td>Niobium</td>
<td>0.0020</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

Fig. 8 displays the XRD patterns of fracture surfaces. Almost the same pattern was obtained in Ti–5Ta alloy and zirconium in both environments. On the other hand, the difference in XRD pattern due to environments was observed in niobium.

In zirconium, basal plane \{0001\} and pyramidal plane \{1011\} were preferentially oriented parallel to the crack propagation direction. In Ti–5Ta alloy, slip planes such as \{1010\}, \{1011\} and \{0001\} had the preferential orientation. In niobium, the preferential orientation was changed from \{110\} in air to \{100\} in nitric acid.

3.3 XRD

Table 2 shows the corrosion rates in boiling 3 kmol/m³ nitric acid obtained from weight loss measurements for Ti–5Ta alloy, niobium, and zirconium. The corrosion rate of Ti–5Ta...
alloy was 0.016 mm/y. It was 20 times higher than that of zirconium.

Figure 9 represents anodic polarization curves measured in boiling 3 kmol/m$^3$ nitric acid. The corrosion potential of zirconium was nobler than that of Ti–5Ta alloy. The passive current density of zirconium was lower than that of Ti–5Ta alloy and niobium. For zirconium, transpassive corrosion occurred above 1.4 V vs. SCE. The general corrosion resistance of zirconium was superior to that of the others.

4. Discussion

4.1 Fatigue crack growth mechanism

The fatigue crack growth rate of zirconium in nitric acid is accelerated with the similar mechanism of SCC due to the pseudo-cleavage type brittle fracture along the basal plane \{0001\}. Figure 10 shows the schematic illustration of the fatigue crack growth mechanism. In static loading mode, the
fluting wall interconnects with the planes ruptured by pseudo-cleavage. Fluting is the result of the slip along the prismatic plane \(\{1010\}\) in the case of SCC.\(^8\) In cyclic loading mode, the fatigue striation caused by slip at crack tip is observed in grains with the crystal orientation unsuitable for pseudo-cleavage cracking. The cracking mode of each grain having a different crystal orientation would be controlled with above two types of crack growth mode: pseudo-cleavage and plastic slip deformation.

In the case of Ti–5Ta alloy, the fatigue crack growth mechanism in nitric acid is similar to that as seen in air. The ductile fracture would be controlled with the plastic deformation on slip planes \(\{1010\}\), \(\{1011\}\) and \(\{0001\}\). In cyclic loading mode, a typical fatigue striation observed in each grain is caused by the formation of the crystal orientation suitable for the plastic deformation as seen in Fig. 8.

In niobium, the fatigue crack growth in nitric acid is controlled with the plastic deformation on slip planes and anodic dissolution from the morphology of the brittle striation in comparison with the ductile striation in air.

### 4.2 Relation between SCC and corrosion fatigue

The SCC of zirconium in nitric acid has been explained with the passive film rupture model according to results of slow strain rate test under polarization and the formation behavior of brittle film.\(^5,6,7,8,9,10,11\) The general corrosion resistance of zirconium is superior to that of Ti–5Ta alloy and niobium on immersion tests. The chemical stability of passive film of zirconium is given in the polarization curve of Fig. 9. The general corrosion resistance of zirconium is better than the others, however transpassive corrosion occurs. These characteristics cause the SCC and corrosion fatigue in nitric acid, thus typical fatigue morphologies. Accordingly, the stability of passive film and the plastic deformation mechanism characterized in the hexagonal close-packed crystal structure described above are possible to cite as the important parameters on the SCC and corrosion fatigue of zirconium.

In Ti–5Ta alloy, the SCC resistance is interpreted to the anodic protection by the chemical dissolution and the difference in the plastic deformation i.e., slip system. The passive film of TiO\(_2\) formed on Ti–5Ta alloy is more stable against localized corrosion than that of ZrO\(_2\) formed on zirconium.\(^10\) As can be seen in Table 3, the slip systems of titanium are \(\{1010\}\), \(\{1011\}\) and \(\{0001\}\), and that of zirconium is only \(\{1010\}\).\(^17,18\) Zirconium and Ti–5Ta alloy used in this study had the same grain size. The plastic deformation occurs more easily than zirconium, because the number of slip systems of titanium is more than that of zirconium.

In the case of niobium, the important factor on the inhibition effect to SCC is the difference in the plastic deformation mechanism due to body-centered cubic crystal structure. Therefore, it is interpreted that the increase of crack growth rate over a wide \(\Delta K\) is caused by corrosion fatigue accelerated by general dissolution as a proof of brittle striations.

### 5. Summary

Fatigue crack growth rates of zirconium, niobium and Ti–5Ta alloy were examined in boiling 3 kmol/m\(^3\) nitric acid and in air at room temperature for evaluating the difference in corrosion fatigue behavior. Following results were obtained:

1. The fatigue crack growth rates of zirconium and niobium in nitric acid showed nearly four times higher than that in air.
2. The acceleration effect of nitric acid was not observed in Ti–5Ta alloy.
3. From the fractography after fatigue tests and the corrosion tests, it was clarified that the transgranular type cracking of zirconium was enhanced in nitric acid.
4. The fatigue crack growth behavior of Ti–5Ta alloy and niobium in nitric acid showed the ductile striation by the transgranular fatigue cracking as seen in air.
5. The fatigue crack growth rate of niobium was promoted in nitric acid by anodic dissolution.

### REFERENCES


<table>
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<tr>
<th>Table 3</th>
<th>Principle slip systems of titanium, zirconium and niobium.</th>
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</thead>
<tbody>
<tr>
<td>Material</td>
<td>Slip plane</td>
</tr>
<tr>
<td>Titanium</td>
<td>{1010}{{1011}{{0001}}</td>
</tr>
<tr>
<td>Zirconium</td>
<td>{1010}</td>
</tr>
<tr>
<td>Niobium</td>
<td>{110}{{112}{{123}}</td>
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