Fatigue crack growth characteristics of nitrogen-alloyed type 347 stainless steel under operating conditions of a pressurized water reactor

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ABSTRACT

The fatigue crack growth behavior of Type 347 (S347) and Type 347N (S347N) stainless steel was evaluated under the operating conditions of a pressurized water reactor (PWR). These two materials showed different fatigue crack growth rates (FCGRs) according to the changes in dissolved oxygen content and frequency. Under the simulated PWR conditions for normal operation, the FCGR of S347N was lower than that of S347 and insensitive to the changes in PWR water conditions. The higher yield strength and better corrosion resistance of the nitrogen-alloyed Type 347 stainless steel might be a main cause of slower FCGR and more stable properties against changes in environmental conditions.

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1. Introduction

The pressurizer surge line, which connects the hot leg pipe to the pressurizer, is used in the highest temperature and pressure of pressurized water reactors (PWRs), at 316 °C and 150 atm. The surge line is known to suffer fatigue damage arising from repeated thermal and mechanical stress, as well as environmental damage due to exposure to the high-temperature and high-pressure cooling-water environment of nuclear power plants. The material for the pressurizer surge line is an austenitic stainless steel, which is known to have excellent corrosion resistance as well as high-temperature strength and fracture toughness [1]. Despite these advantages, the long-term use of austenitic stainless steel at high temperature can lead to sensitization, which involves the formation of metal carbides (M23C6) and depletion of grain-boundary chromium [2]. The use of carbon-reduced Type 304L stainless steel is known to be effective in reducing the sensitization of austenitic stainless steel, but the reduced carbon content is accompanied by a decrease in high-temperature mechanical strength [2,3].

When the amount of carbon decreases, austenitic stainless steel tends to show an enhanced sensitization resistance and fracture toughness but a weaker mechanical strength. Recently, nitrogen-added austenitic stainless steel has been studied to improve both the mechanical strength owing to precipitation strengthening [2,3] and the corrosion resistance properties [4–7]. However, previous investigations were focused on the stress corrosion cracking [2,8–13] of nitrogen-alloyed Type 304 and 316 stainless steel in chloride solutions and under boiling water reactor environments. There is a lack of research on the fatigue crack growth rate (FCGR) in PWR environments. In the case of Korea Standard Nuclear Power Plant, Type 347 stainless steel is used in pressurizer surge line because higher strength and toughness at high temperature are required to improve a design margin based on the LBB (leak-before-break) concept. Several studies were carried out to improve the fracture toughness and strength of Type 347 stainless steels, but studies on the FCGR in PWR water conditions are very few.

In this study, the FCGR of Type 347 stainless steel, with and without addition of nitrogen, was evaluated in PWR high-temperature water conditions. The FCGRs of Type 347 stainless steel and Type 347N stainless steel under pressurized-water conditions were measured using compact-tension specimens at different levels of dissolved oxygen (DO) and frequency. The effects of adding nitrogen to Type 347 stainless steel were examined through the FCGR data and microstructural observations.

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2. Materials and methods

2.1. Materials and specimens

The materials used in this study were a commercial Type 347 stainless steel (S347) and a Type 347N stainless steel (S347N) model alloy that was produced by pressurized melting with the addition of 0.11 wt.% of nitrogen. The chemical composition of the materials is given in Table 1. Prior to the experiment, each material was homogenization annealed at 1,050 °C for 1 hour. The overall microstructures were compared through observations via an optical microscope (Eclipse MA200; Nikon, Tokyo, Japan), a field-emission scanning electron microscope (FE-SEM; S-4800; Hitachi, Tokyo Japan), and a transmission electron microscope (FB-2100; JEOL Ltd, Tokyo, Japan). The specimens used in the tensile tests were in the form of rods with a gauge length of 25 mm and a diameter of 6.35 mm. In accordance with American Society for Testing and Materials (ASTM) E8 [14], tensile tests were carried out at room temperature (RT) and 316 °C with a strain rate of 5.2 × 10⁻⁴ s⁻¹.

2.2. FCGR tests under PWR water conditions

The FCGR tests were performed on precracked compact-tension specimens with a width of 25.4 mm and a thickness of 5 mm [orientation: transverse—longitudinal (T–L)]. The initial crack size was approximately 0.24 of the specimen width. As shown in Fig. 1, measurements of FCGR under PWR water conditions were carried out using a fatigue testing machine (8502; Instron, Norwood, MA, USA), which comprised a water chemistry control loop and a high pressure—temperature autoclave. A pressure balance was attached to compensate for the effects of the internal pressure on the load cell signal outside the autoclave. The PWR water conditions—DO level, dissolved hydrogen (DH) level, pH, and conductivity—were controlled using the loop system. PWR water conditions under normal operation were simulated using ultrapure water with reagent concentrations of dissolved oxygen (DO, 5 ppb and 100 ppb), dissolved hydrogen (DH, 1 ppb), pH of 7.0, and conductivity of 15–17 MΩ cm. The oxidized water was preheated and entered the autoclave where the test solution was cooled on the downstream and returned to the feed tank. The electrochemical corrosion tests were conducted at 316 °C under 15 MPa. The DO concentrations were maintained at 5 ppb and 100 ppb. The potentiodynamic polarization tests were carried out using the potentiotstat. An Ag/AgCl electrode and a platinum wire were used as a reference and counter electrode, respectively. Each exposed surface area of the S347 and S347N specimens was 2 cm².

3. Results

3.1. Microstructures

The microstructures of S347 and S347N were compared using optical microscopy, as shown in Fig. 2. The grain sizes were measured using the intersection method described in ASTM E1382 [16]. The grain size of S347 was 42 μm, whereas that of the nitrogen-alloyed S347N was smaller at 28 μm. Images obtained from FE-SEM analysis for the precipitation behavior are shown in Fig. 3. For S347, the more medium-sized precipitates were uniformly distributed. The nitrogen-alloyed S347N showed coarse precipitates along the rolling direction. The microstructures of S347 and S347N were observed using a transmission electron microscope, and the images of S347N are shown in Fig. 4. Analysis of the selected-area diffraction patterns was used to identify the precipitates of S347 and S347N as niobium carbide (NbC) and niobium nitride (NbN) (collectively abbreviated hereafter as Nb(C, N)).

3.2. Tensile properties

The stress—strain curves of the tensile properties of S347 and S347N are shown in Fig. 5. The yield strength, tensile strength, and elongation of the two materials are listed in Table 3. The yield strength was measured using the 0.2% offset method. The addition of nitrogen increased the yield strength and tensile strength, but it decreased the elongation at RT. The yield strength, tensile strength, and elongation of all materials at 316 °C showed a tendency to decrease from those at RT. The tensile properties of S347N were superior to those of S347 at all test temperatures. The increase in strength at both temperatures was caused by hardening of Nb(C, N) precipitates in S347N. Serration was observed in the strain—stress curve at 316 °C, as shown in Fig. 5, and its effects were more severe in S347N. It is considered that serration is induced by the effects of dynamic strain aging. Thus, the large decrease in elongation of S347 at 316 °C may have been due to the effects of dynamic strain aging.

3.3. Evaluation of FCGR at higher frequency

Fig. 6 shows the FCGR test results for S347 and S347N under the PWR water conditions at two different DO levels and a frequency of 10 Hz. For comparison, the American Society of Mechanical Engineers (ASME) code section XI curves in air [17] corresponding to each temperature are represented by the dotted lines in Fig. 6. The FCGRs of S347N were lower than those of S347 at 5 ppb (Figs. 6A and 6B). The FCGRs of both materials did not significantly change regardless of the test temperature. However, at 100 ppb and 316 °C, the FCGRs of S347 were lower as indicated in Fig. 6D. Unlike the results at 5 ppb and 316 °C, the FCGRs of S347 significantly decreased at 100 ppb and 316 °C when compared to the results at 100 ppb and 25 °C. In the case of S347N, however, the FCGRs were similar under all test conditions. Compared to the ASME curves, the FCGRs of S347 and S347N are similar or slightly lower at all test conditions.
Normally, in the stage II region of the FCGR curve, the relationship between the FCGR and \( \Delta K \) is represented by Paris’ equation, as shown in Eq. (1):

\[
\frac{da}{dN} = C(\Delta K)^n
\]  

(1)

The FCGR is defined as the derivative, \( \frac{da}{dN} \), on the left side of Eq. (1), where \( a \) is the crack length and \( N \) is the number of loading cycles. Least-squares fitting was used to derive the scaling constants \( C \) and exponents \( n \) from the \( \frac{da}{dN} \) curves at each level of DO and temperature; the results are listed in Table 4. Except for the result for S347 at 100 ppb and 316°C, the exponents \( n \) were similar in a range of 5.2–5.6. Although there was a difference between the values of the exponent in the data and the ASME curves \( (n = 3.3) \), the overall trend of \( n \) value was not much changed by the environment for each material. Regardless of the temperature and DO level, the \( C \) value of S347N was lower than that of S347.

### 3.4. Evaluation of FCGR at lower frequency

The effects of PWR environmental conditions on FCGR may be enlarged in lower frequency tests than higher frequency [18]. As the frequency increases, the crack tip opening time (CTOT) decreases and the crack tip is less affected by the chemistry of PWR water. Thus, corrosion effects on fatigue crack growth are relatively small.
and the mechanical effects are dominant [18]. Therefore, FCGR tests should be carried out at lower frequency to analyze the effects of corrosion under normal operating conditions [19]. Fig. 7 presents a comparison of the FCGRs of the two materials at a low frequency of 0.1 Hz. As the frequency decreased, the FCGR of S347 increased at all DO levels, and the increase was especially pronounced at a higher DO level of 100 ppb. However, the FCGR of S347N did not show a significant change despite the decrease in frequency at each DO level (Fig. 7B).

3.5. Observation of fatigue crack surface

Figs. 8 and 9 show FE-SEM images of the fatigue crack surface and oxide layer of S347 and S347N after the FCGR tests. Oxide particles were not observed regardless of the DO level at 25 °C, but polyhedral oxide particles were observed in both materials at all DO levels of 5 ppb and 100 ppb at 316 °C. In the case of S347, the size of oxide particles increased from 0.2 μm to 1 μm as the DO level increased. However, the size of oxide particles in S347N remained at 0.2 μm regardless of the DO level.

Table 3

<table>
<thead>
<tr>
<th></th>
<th>Room temperature (25 °C)</th>
<th>316 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YS (MPa)</td>
<td>UTS (MPa)</td>
</tr>
<tr>
<td>S347</td>
<td>242 (±1.80)</td>
<td>657 (±1.30)</td>
</tr>
<tr>
<td>S347N</td>
<td>300 (±1.50)</td>
<td>671 (±1.10)</td>
</tr>
</tbody>
</table>

Values within parentheses are standard deviation. EI, elongation; UTS, ultimate tensile strength; YS, yield strength.

Cross-sectional images of the tested specimens are shown in Fig. 10, where the thickness of the oxide layer is indicated by the distance between the white dotted lines (location: near Δk = 25 MPa m1/2). The thicknesses of the oxide layer of S347 were 1.65 μm and 3.62 μm at 5 ppb and 100 ppb, respectively. However, the oxide layer of S347N was 1.65 μm thick at both DO levels. The size of the oxide particles and the thickness of the oxide layers were almost identical regardless of frequencies (0.1 Hz or 10 Hz) at each DO level. The compositions of the oxides were analyzed using X-ray photoelectron spectroscopy and the results are shown in Fig. 11 [20]. According to the analysis of the binding energy of Fe, oxides and oxide layer were defined as Fe3O4 [21].

4. Discussion

4.1. Effects of yield strength

It has been reported that the FCGR is generally affected by the yield strength [22]. The plastic-zone size decreases when the yield strength increases, and this increases the resistance to fatigue crack growth. The addition of nitrogen increases the yield strength owing to grain refinement, precipitation hardening, and solid-solution hardening, which in turn, decreases the FCGR [23]. The FCGR of S347N was lower than that of S347 regardless of the DO levels at 25 °C. FE-SEM results comparing the fatigue crack surface at 25 °C showed that oxide particles were not present at any DO level (Figs. 8A and 9A). Therefore, the FCGR at 25 °C was mostly affected by changes in the mechanical properties of materials rather than by the level of DO. According to Lee et al [24], precipitates do not affect the FCGR in the steady growth stage of a fatigue crack. However, in this study the addition of nitrogen produced Nb(C, N), enhancing the yield strength, which in turn decreased the FCGR. The strengthening phenomena due to solid-solution hardening, precipitate hardening, and grain refinement, might have decreased the FCGR of S347N.

4.2. Effects of corrosion

The FCGRs of S347 were found during the experiment to depend...
on the frequency and the DO level. Unlike the other conditions, the FCGR remarkably decreased when the DO level was increased to 100 ppb at a high frequency of 10 Hz. It was observed that the size of oxide particles and the oxide-layer thickness were much higher at a DO level of 100 ppb. It is known that oxide particles formed at crack tips can induce the crack-closure phenomenon at low ΔK levels [25, 26]. In our study, coarse oxide particles formed at the crack tip in S347 caused the crack-closure phenomenon; this decreased the FCGR at 100 ppb of DO and 10 Hz. However, the oxide formed at a DO level of 5 ppb was small in size, and the small oxide particles did not significantly affect the crack-closure phenomenon.

At higher frequency (10 Hz), the chemical environment of PWR water may not have enough time to react with the crack tip during each load cycle. Thus, the effects of the water chemical environment on the fatigue crack growth were not significant [18], and the mechanical effect of crack closure became relatively intensive. At lower frequency (0.1 Hz), the FCGR of S347 was completely different from the result at high frequency. The FCGR of S347 remarkably increased at 316°C and 0.1 Hz, as shown in Fig. 7, whereas S347N did not show a substantial change. The CTOT increased at low frequency, exposing the crack tip to the PWR water conditions for a longer period, and it increased the FCGR [27].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temp (°C)</th>
<th>DO (ppb)</th>
<th>C (mm/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S347</td>
<td>25</td>
<td>5</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5.2</td>
<td>$2.24 \times 10^{-11}$</td>
</tr>
<tr>
<td>S347N</td>
<td>25</td>
<td>5</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5.6</td>
<td>$7.94 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

**Table 4**

Paris' law constant determined from the FCGR test results under different PWR water conditions.

DO, dissolved oxygen; FCGR, fatigue crack growth rate; PWR, pressurized water reactor.

![Fig. 6](image_url)

Effects of dissolved oxygen (DO) on fatigue crack growth rates of S347 and S347N under different PWR water conditions (pressure, 15 MPa; frequency, 10 Hz). (A) DO < 5 ppb (25°C). (B) DO < 5 ppb (316°C). (C) DO = 100 ppb (25°C). (D) DO = 100 ppb (316°C). The dotted lines are the American Society of Mechanical Engineers (ASME) Code reference curves in air environment.

![Fig. 7](image_url)

Effects of frequency on fatigue crack growth rate of stainless steel under different PWR water conditions (pressure, 15 MPa; temperature, 316°C). (A) S347. (B) S347N. DO, dissolved oxygen.
Similar results have been reported, in which the fatigue life decreased with a decrease in the strain rate in low-cycle fatigue life assessments in PWR water environments [27,28]. However, the FCGR of S347N did not change much despite the decrease in frequency at both DO levels. Therefore, the noticeable increase in the FCGR of S347 compared to S347N at low frequency suggests that it may have been caused by the corrosion characteristics of each material. The increase in DO level increased the size of the oxide particles and the oxide-layer thickness in S347, indicating that S347 was more sensitive to changes in the PWR water conditions.

To compare the corrosion properties of both materials, electrochemical evaluations were performed, and the results are shown in Fig. 12. In S347, the electrochemical potential (ECP) increased as the DO level was increased. However, there was no change in the ECP in S347N. It was reported that the DO level significantly affects the ECP of the material under PWR water conditions [29]. When the ECP increases with the DO level, the crack growth rate can also increase. It is well known that the ECP directly affects the corrosion rate of a material [30].

The corrosion rate of the materials under each condition was calculated by Tafel extrapolation, and the results are shown in Table 5. As the DO level was increased from 5 ppb to 100 ppb, the corrosion rate of S347 increased from 2.15 mpy (mil penetration per year) to 3.80 mpy, whereas that of S347N remained at 2.22–2.38 mpy. This result suggests that the FCGR of S347 increased owing to the elevated corrosion rate at 100 ppb and 0.1 Hz. By contrast, owing to improved corrosion resistance, the FCGRs of S347N were not much changed as DO and frequency were varied. In general, when nitrogen is added to austenitic stainless steel, NO₃⁻ and NO₂⁻ ions, which are known to be corrosion inhibitors, are produced within the solution [5]. Moreover, nitrogen ions are formed in a passive layer, preventing oxygen bonding and delaying the oxidation process [30]. Hence, the oxide particle size and oxide-layer thickness of S347N did not change despite the increase in DO level. The addition of nitrogen to Type 347 enhanced both the yield strength and corrosion resistance, and it kept the FCGR stable under the PWR environmental changes.

5. Conclusion

In this study, the FCGRs of Type 347 and Type 347N stainless steel were evaluated under simulated PWR water conditions according to various environmental parameters such as temperature, DO concentration, and frequency. The findings are summarized as follows: (1) Grain refinement and precipitation hardening by nitrogen addition in S347N increased its yield strength. At low temperature (25°C), at which oxide particles were not formed, the FCGR of S347N was lower than that of S347 regardless of the DO level under various PWR water conditions owing to the higher yield strength. (2) Under high-temperature (316°C) PWR water conditions, oxide particles were formed at crack surfaces in both specimens. However, the corrosion rates of S347 and S347N differed.
Fig. 10. Cross-sectional images of FCGR test specimens under PWR water conditions (pressure, 15 MPa; frequency, 10 Hz). (A) S347, DO < 5 ppb. (B) S347, DO = 100 ppb. (C) S347N, DO < 5 ppb. (D) S347N, DO = 100 ppb. The thickness of the oxide layer is indicated by the distance between the dotted lines. DO, dissolved oxygen; FCGR, fatigue crack growth rate; PWR, pressurized water reactor.


Fig. 12. Potentiodynamic polarization curves of stainless steels in 0.001M NaOH solution at different DO levels under PWR water conditions (pressure, 15 MPa; DO, 5 ppb and 100 ppb; temperature, 316°C). (A) S347. (B) S347N. A standard hydrogen electrode (SHE) was used as the reference electrode. DO, dissolved oxygen; PWR, pressurized water reactor.
with changes in the DO levels. When the DO level was increased, the corrosion rate of S347 increased, whereas that of S347N remained almost unchanged. The corrosion resistance of S347N was superior to that of S347. (3) Under high-temperature PWR water conditions, the FCGR of S347 was significantly affected by changes in the DO level and frequency. At a high frequency of 10 Hz, the FCGR decreased as the DO level was increased because the coarse oxide particles formed at the crack tip caused the crack-closure effect. However, at a low frequency of 0.1 Hz, the FCGR of S347 significantly increased as the DO level was increased because the effect of corrosion on material degradation increased as the CTOT increased. (4) Under simulated PWR conditions for normal operation, the FCGR of S347N was lower because of its higher yield strength. The FCGR of S347N did not change much regardless of the changes in PWR water conditions because of the superior corrosion resistance of S347N. In conclusion, Type 347N stainless steel showed a promising fatigue crack growth resistance under high-temperature water conditions through the hardening effects and enhanced corrosion resistance compared to normal Type 347 stainless steel.

Conflict of interest

The researcher claims no conflicts of interest.

Acknowledgments

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References