Characteristic Fatigue Crack Growth Behavior of Low Carbon Steel under Low-pressure Hydrogen Gas Atmosphere in an Ultra-low Frequency

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In order to clarify an influence of hydrogen on the fatigue crack propagation in ultra-low frequency region, we investigated the crack propagation rates of S10C at different frequencies in hydrogen and nitrogen atmospheres. In the low-pressure hydrogen gas atmosphere, the crack propagation rate decreased with decreasing in frequency within the present experimental range. In particular, the crack propagation rate at the ultra-low frequency (10⁻³ Hz) became the same as that in nitrogen atmosphere. To explain the disappearance of the hydrogen effect in the ultra-low frequency, we proposed that carbon diffusion causing strain-age hardening also contributes to the decrease in crack propagation rate in the ultra-low frequency under the hydrogen atmosphere.

KEY WORDS: fatigue crack growth; hydrogen gas atmosphere; frequency dependency; low carbon steel; pre-cracked specimen.

1. Introduction

An evaluation of the mechanical properties of hydrogen carriers under a hydrogen atmosphere is required in order to develop hydrogen energy applications. Hydrogen degrades the mechanical properties of iron and steel,1–6) and therefore an understanding of resistance to hydrogen embrittlement is an indispensable and practical issue. In particular, ferritic and martensitic steels exhibit high susceptibility to hydrogen embrittlement because of two factors: 1) their usage under high-stress conditions, and 2) the relatively high diffusion rate of hydrogen compared to that of FCC materials. More specifically, the tensile property and fatigue crack growth property of steels1,3,5,6) are critically degraded due to hydrogen.

Fatigue damage is generally crucial for accidental failure including hydrogen-related fracture. In order to confirm the reliability of steel structures, it is necessary to evaluate the fatigue properties in various hydrogen atmospheres with different temperatures, frequencies, and pressure conditions. In particular, a fueling/defueling cycle in a hydrogen gas storage tank is estimated to require more than a day.7) Hydrogen storage tanks are exposed to fatigue conditions with a much lower frequency than those employed in general fatigue tests. It has been reported that hydrogen embrittlement susceptibility increases with decreasing deformation speed.3,8–11) Hence, the practical use of steels for hydrogen storage tanks exposed to ultra-low frequency conditions presents a significant risk in terms of fatigue failure, which cannot be predicted by fatigue testing under standard frequency conditions.

Regarding the frequency dependence of the fatigue damage evolution of steels in terms of the effect of hydrogen on the fatigue crack propagation rate, it has been reported that the fatigue crack propagation rates increase with decreasing frequency.12–16) According to these reports, the hydrogen gas fatigue test frequency affects dislocation mobility at the fatigue crack tip1; hydrogen uptake/diffusion behavior,12,13) impurity diffusion in the hydrogen atmosphere.16) Moreover, the degree of the negative effect of frequency on fatigue crack propagation behavior changes with the chemical composition and test conditions. Because of this complexity, the actual effect of frequency on fatigue crack growth in a hydrogen atmosphere is still under discussion.

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*1 Since dislocation mobility is generally controlled by the Peierls potential and thermally activated processes, dislocation mobility increases with decreasing strain rate at a crack tip, which corresponds to the frequency. Since the Peierls potential is independent of frequency, thermally activated processes cause the frequency dependence of the fatigue crack growth rate. Namely, dislocation slip occurs more easily with decreasing frequency, increasing the fatigue crack growth rate. However, in real materials such as steels, which contain interstitial atoms, the kinetics of solute atom diffusion, e.g. dynamic strain aging, affect the dislocation mobility. The kinetics of solute atom diffusion causes the negative frequency dependence of the dislocation mobility.11–19) Since dynamic strain aging is one of the important factors that control fatigue crack propagation behavior,20,21) when it occurs, the fatigue crack growth rate exhibits a negative frequency dependence in response to the change in dislocation mobility.
As mentioned above, a decrease in frequency in a hydrogen atmosphere has been reported to increase hydrogen embrittlement susceptibility, accelerating the fatigue crack propagation rate. However, it has recently been reported that the fatigue crack propagation rate of carbon steels decreases with decreasing frequency, in a compact tension (CT) experiment satisfying a small-scale yield condition at a stress ratio of 0.1.\textsuperscript{22)} This result is important in terms of certain design strategies for materials used in low-frequency fatigue conditions such as hydrogen storage tanks. Therefore, in order to investigate the availability of this phenomenon, the effect of ultra-low frequencies must be evaluated in a variety of conditions. For example, in the majority of cases, surface scratches are introduced in the production process and in service. In addition, materials that are used in practice contain a large amount of inclusions. Most of the fatigue cracks that initiate from these surface scratches and inclusions do not satisfy the small-scale yield condition. In other words, we have to specifically simulate fatigue crack growth that stems from surface scratches or inclusions in parts of real structures. For instance, fatigue testing of a specimen that contains a micro-scale artificial flaw is a possible experimental method for evaluating the effect of defects in parts of real structures.

In this paper, we focus on fatigue characteristics at low frequencies, where the fatigue crack propagation rate was reported to decrease with decreasing frequency in annealed carbon steel with a ferrite/pearlite microstructure. In particular, we discuss the fatigue crack propagation behavior initiating from an artificial defect at an ultra-low frequency under a hydrogen gas atmosphere. The emphasis of this study is placed on the following points.

1) We observed the surface fatigue crack propagation rate in a hydrogen atmosphere, and accordingly measured the frequency dependence of the fatigue crack propagation behavior through fully reserved bending fatigue testing (at a stress ratio of \(-1\)). A deceleration of the fatigue crack propagation rate with decreasing frequency was observed in this experiment under a hydrogen environment.

2) By correlating fractographic analysis with the observed fatigue crack propagation behavior, we clarified the cause of the frequency dependence of the fatigue crack propagation rate under a hydrogen gas environment.

2. Experimental Procedure

Low carbon steel (JIS S10C) was used in this study. Table 1 shows the chemical composition of the low carbon steel. Figure 1 shows the microstructure of the as-annealed steel. The microstructure was obtained by mechanical polishing and subsequent chemical etching with 3% Nital. The initial structure consisted of ferrite with a small amount of pearlite. The ferrite grain size was approximately 25 \(\mu m\). A cylindrical bar with a diameter of 22 mm was annealed at 1,173 K for 1 h and then furnace-cooled to room temperature. Table 2 shows the tensile mechanical properties of the steel. Testing was conducted at a nominal strain rate of \(10^{-2} \text{ s}^{-1}\) at room temperature. In order to introduce trap sites for hydrogen such as dislocations, fatigue test specimens were 10%-pre-strained using tensile deformation. Figure 2(a) shows the specimen configuration for fatigue testing. The specimen surface was polished with #2000 emery paper and subsequently buff-polished using alumina particles with a diameter of 50 nm in order to simplify the surface observations. Figure 2(b) shows the geometry of the artificial flaw that was introduced by micro-drilling at the center of the specimen. The drill holes were perpendicularly aligned along the longitudinal direction of the specimen.

All fatigue tests were conducted using a triangle test wave and a fully reserved bending condition. Figure 2(c) shows a schematic illustration of the loading direction. Test frequencies of 6, \(5 \times 10^{-3}\), and \(1 \times 10^{-3} \text{ Hz}\) were used. In this study, 1 \(\times 10^{-3}\) Hz was the lowest frequency that was adopted. However, since the minimum frequency of the stepping motor used was \(4 \times 10^{-3} \text{ Hz}\), in order to obtain a frequency of \(1 \times 10^{-3} \text{ Hz}\), a frequency of \(4 \times 10^{-3} \text{ Hz}\) was repeatedly used for 0.37 s, in conjunction with a displacement holding of 1.07 s. This combined frequency test condition is defined as a frequency of \(1 \times 10^{-3} \text{ Hz}\) in the present study. In order to remove any effects of the shape of the crack starter on

<p>| Table 1. Chemical composition of S10C (mass%). |
|---|---|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Al</th>
<th>Ni+Cr</th>
<th>Fe</th>
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<tr>
<td>0.13</td>
<td>0.22</td>
<td>0.39</td>
<td>0.01</td>
<td>0.02</td>
<td>0.09</td>
<td>0.01</td>
<td>0.01</td>
<td>Bal.</td>
</tr>
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</table>

<p>| Table 2. Tensile properties of the steel used. |
|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>Upper yield strength</th>
<th>Lower yield strength</th>
<th>Ultimate tensile strength</th>
<th>Total elongation</th>
</tr>
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<tbody>
<tr>
<td>223 MPa</td>
<td>207 MPa</td>
<td>352 MPa</td>
<td>33%</td>
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Fig. 1. Undeformed microstructure of the steel used. The black region is pearlite, and the other region is ferrite.
fatigue crack propagation, we focused on fatigue crack propagation after 700 $\mu$m of crack growth, which is sufficiently larger than the size of the crack starter. When testing was performed at $1 \times 10^{-3}$ Hz, the initial frequency was 6 Hz, and the frequency was then changed to $1 \times 10^{-3}$ Hz at a crack length of 700 $\mu$m in order to shorten the testing time. In this study, the crack length, $l$, is the projection length that includes the size of the coupled two drilled holes. The test atmosphere was 99.9999% pure hydrogen gas at 313 K and 0.18 MPa (absolute pressure). We observed fatigue crack propagation over the pressure chamber using an optical microscope. The total strain range, $\Delta \varepsilon$, was 0.70%. The strain range was guaranteed by using a strain gauge that was pasted onto the center of the reverse side of the specimen. In order to homogenize conditions such as hydrogen distribution and specimen temperature at the initial stage of fatigue testing, we exposed the specimen to the test gas at 0.18 MPa and 313 K for 1 h before testing. We also carried out the same experiment in nitrogen gas, for comparison. Furthermore, after the observation of fatigue crack propagation, specimens were fractured by hammering after immersion in liquid nitrogen in order to observe the fracture surface. The fracture surface was observed using scanning electron microscopy (SEM).

3. Results and Discussion

3.1. Atmosphere and Frequency Dependences of Fatigue Crack Propagation Behavior

Figure 3 shows the fatigue crack propagation behavior in hydrogen and nitrogen gas atmospheres at frequencies of 6 Hz. The x-axes of Figs. 3(a) and 3(b) refer to the total and partial number of cycles from a crack length of 700 $\mu$m, respectively. Figure 3(b) is presented for comparison with Fig. 4, where the number of cycles was also counted from a crack length of 700 $\mu$m. In the tests performed at 6 Hz, the fatigue crack growth rate in hydrogen was higher than that in $N_2$. Hydrogen has been known to significantly increase dislocation mobility, which locally accelerates plastic deformation in the hydrogen-affected zone (referred to as hydrogen-enhanced localized plasticity: HELP).\(^{17}\) The acceleration of fatigue crack propagation in the hydrogen atmosphere at 6 Hz can be explained by microvoid formation and subsequent coalescence with the crack tip that is associated with the HELP effect.\(^{23,24}\)

Figure 4 shows the fatigue crack propagation behavior in hydrogen and nitrogen gas atmospheres at a test frequency of $1 \times 10^{-3}$ Hz. In the tests at $1 \times 10^{-3}$ Hz, the fatigue crack growth rate in hydrogen was nearly equal to that in nitrogen. In other words, the hydrogen-accelerated fatigue crack growth disappeared when the frequency was reduced from 6 to $1 \times 10^{-3}$ Hz. In order to discuss the disappearance of the HELP effect, Figs. 5 and 6 show the fatigue crack propagation behaviors in $H_2$ and $N_2$ gas atmospheres at different test frequencies: 6, $5 \times 10^{-3}$, and $1 \times 10^{-3}$ Hz. In the nitrogen gas atmosphere, the fatigue crack growth rate increased with a drop in the frequency. In contrast, the fatigue crack growth rate in the hydrogen gas atmosphere decreased with a drop in the frequency. Namely, the frequency dependence of the fatigue crack growth rate in hydrogen was the inverse of that of nitrogen. It is considered that strain aging of carbon, accompanied by deformation localization, is a cause of the negative frequency dependence of the fatigue crack growth rate in a nitrogen gas atmosphere. Since the strain rate in the vicinity of the crack tip decreases with decreasing frequency, dynamic strain aging occurs more easily. When dynamic strain aging occurs, plastic deformation is localized due to dislocation depinning from carbon atmosphere. In tensile tests, this phenomenon is referred to as Portevin-Le Chatelier banding.\(^{25}\) The plastic strain localization in the vicinity of the crack tip contributes to the acceleration of
fatigue crack propagation. In contrast, hydrogen distribution is the primary factor affecting the frequency dependence of the fatigue crack growth rate in the hydrogen gas atmosphere. Hydrogen is known to localize at a crack tip, promoting fatigue crack propagation associated with HELP.\(^{26,27}\) However, for extremely low frequencies such as \(1 \times 10^{-3}\) Hz in ferrite, hydrogen can diffuse from the crack surface to regions beyond the vicinity of the crack tip. The extent of the hydrogen-affected zone implies that homogenization of hydrogen distribution in the vicinity of the crack tip, and accordingly, the HELP effect, may be suppressed.\(^{22}\) Nevertheless, the disappearance of the acceleration effect of hydrogen on fatigue crack growth rate at ultra-low frequencies cannot be explained merely in terms of the simple effect of hydrogen homogenization at the crack tip. This is discussed in more detail in the following section in terms of the results for fatigue cracking on fracture surfaces.

3.2. Analysis of the Fatigue Crack Propagation Path and Fracture Surface

First, we discuss hydrogen-accelerated fatigue crack growth at a test frequency of 6 Hz. In fact, a change in the crack propagation mode is a cause of the acceleration of the fatigue crack propagation in S10C together with an effect related to hydrogen. The transition of the fatigue crack propagation mode provides brittle striation.\(^{23}\) Figure 7 shows that approximately 80% of the fracture surface in hydrogen at 6 Hz is occupied by a region that exhibits brittle striation. The fatigue crack propagation mode with brittle striation arose from HELP-related hydrogen-assisted microvoid formation at the crack tip and its subsequent coalescence with the main crack.\(^{23,24}\) On the other hand, hydrogen hardly affected the fatigue crack growth rate at a test frequency of \(1 \times 10^{-3}\) Hz. In order to interpret the disappearance of the effect of hydrogen at the ultra-low frequency, this phenomenon is expounded using the following two routes of discussion.

I) Although the acceleration effect of hydrogen exists even at the ultra-low frequency, the fatigue crack growth rate did not apparently change. Zigzag crack propagation decreases the crack growth rate that is calculated from projection crack length. Assuming that the hydrogen causes the zigzag crack propagation, this deceleration effect on the crack growth due to the hydrogen would compete with the acceleration of crack growth that is probably due to the HELP effect.

II) The HELP effect does not affect the fatigue crack growth rate at the ultra-low frequency because the hydrogen distribution is relatively homogenized.

From the viewpoint of route I), the fatigue crack propagation path can be explained by means of in-situ observations. Figure 8 shows micrographs indicating the fatigue crack propagation paths in nitrogen and hydrogen gas atmospheres. The fatigue cracks are underlined using red lines. Figure 8 indicates that hydrogen did not play a significant role in changing the propagation path to a zigzag path. This result indicates that route I) does not provide the main reason for the disappearance of the acceleration effect of hydrogen on the fatigue crack growth. In other words, route II), which is associated with a reduced HELP effect, may be
used when considering the disappearance of the acceleration effect of hydrogen on the fatigue crack growth rate.

In order to consider a reason for the disappearance of the HELP-related acceleration effect of hydrogen, the fracture surfaces were observed, as shown in Fig. 9. The drill holes shown in the lower part of Fig. 9 were those used as the crack starter (compare with Fig. 8). In addition, the broken yellow lines in the central part indicate the position at which the test frequency was changed (6 Hz → $1 \times 10^{-3}$ Hz). Figure 10 shows a magnified image of the region outlined by a yellow dotted line in Fig. 9(a). The fracture surface image obtained after fatigue at a test frequency of $1 \times 10^{-3}$ Hz in nitrogen indicates a ductile fatigue feature that includes general ductile striations. With reference to the fractographic features in the nitrogen gas atmosphere, we evaluated the fracture surface at $1 \times 10^{-3}$ Hz in the hydrogen gas atmosphere. Figure 11 shows a magnified image of the left part of Fig. 9(b). The same ductile feature as was exhibited in nitrogen also appears in Fig. 11(a). Compared with the brittle-like fracture surface containing brittle striations that was observed at 6 Hz in hydrogen, the suppression of HELP-related microvoid formation/coalescence at the crack tip appears to be the major factor that reduced the acceleration effect of hydrogen on fatigue crack growth at a frequency of $1 \times 10^{-3}$ Hz. As mentioned in the previous section, hydrogen distribution at the crack tip can be relatively homogenized at frequencies low enough to provide sufficient time for hydrogen diffusion. This phenomenon is considered to reduce the HELP effect at the crack tip. Accordingly, the acceleration effect of hydrogen on fatigue crack growth rate is reduced. However, the “disappearance” of the acceleration effect of hydrogen, namely, the fact that the fatigue crack growth rates in hydrogen were nearly equal to those in nitrogen, cannot be explained using only the effect of hydrogen homogenization. We must consider the underlying mechanism of the disappearance of the HELP-related acceleration of fatigue crack growth.

3.3. Proposal of an Influence of Carbon Diffusion in the Hydrogen Atmosphere

As mentioned in the previous section, in addition to the influence of hydrogen homogenization at the crack tip, an extra factor is required in order to fully understand the mechanism behind the disappearance of the acceleration effect of hydrogen on fatigue crack growth at lower frequencies. This extra factor is required for the following reasons.

1) Figure 11(b) shows a magnified image of the right part of Fig. 9(b). The formation of brittle striations was observed in part. This implies that the fatigue crack growth rate in the region where brittle striations were formed must have been higher than it would have been without the effect of hydrogen.

2) Even if hydrogen distribution was completely homogenized, fatigue crack growth must accelerate more or less in a manner related to hydrogen-enhanced plasticity.

3) Because of the stress gradient at the crack tip in the crack opening process, hydrogen heterogeneity at the crack tip cannot completely disappear.

4) A considerable amount of dislocations appears in the vicinity of the crack tip because of plastic strain concentration. Since dislocations are typical trap sites for hydrogen, the amount of hydrogen at the fatigue crack tip is considered to be larger than that in the smooth region.

Hence, a comprehensive understanding of the “disappearance” of the acceleration effect of hydrogen on the fatigue crack growth at the ultra-low frequency cannot be achieved by considering only the effect of hydrogen homogenization at the crack tip. In order to elucidate this effect at the ultra-low frequency, we suggest an effect related to carbon diffusion.

Fig. 9. Overviews of the fracture surfaces provided at 0.001 Hz in (a) nitrogen and (b) hydrogen gas atmospheres. The broken lines indicate the changing points of frequency from 6 to $10^{-3}$ Hz ($l=700 \, \mu m$).

Fig. 10. Magnified image of the region outlined by the yellow broken lines in Fig. 9(a).

Fig. 11. Magnified image of the region outlined by the yellow broken lines in Fig. 9(b). (a) Ductile striations. (b) Brittle striation as indicated by the yellow arrows.
diffusion at the crack tip. The presence of diffusible solute elements such as carbon in steel is well known. In the case of a test frequency of $1 \times 10^{-3}$ Hz, the time required for 1 cycle of fatigue crack opening and closing is $1 \times 10^3$ s. Since significant strain-age hardening in carbon steel occurs within $1 \times 10^3$ s at 40°C, which corresponds to the present experimental condition, the effect of carbon diffusion is expected to contribute to a decrease in the fatigue crack propagation rate at a frequency of $1 \times 10^{-3}$ Hz. Considering that carbon segregation occurs in dislocations, we assert that the following two factors affect hydrogen distribution and fatigue crack propagation.

A) Carbon segregation to a dislocation or its vicinity facilitates hydrogen desorption from the dislocation because of a reduction in the trapping energy of hydrogen. A dislocation is a weak trap site, and thus, trapped hydrogen is diffusible. This indicates that hydrogen repeatedly segregates to and escapes from dislocations. On the other hand, carbon is not easily desorbed from a dislocation after segregation, which indicates that more carbon remains in the dislocations compared to hydrogen after a sufficient time for carbon diffusion to a dislocation is given. Hence, this phenomenon may be considered to suppress the HELP effect.

B) Fatigue crack propagation can be prevented by strain-age hardening associated with carbon segregation to a dislocation at the crack tip. In Nishikawa’s model, hydrogen segregation in front of a crack tip causes plastic strain localization, resulting in microvoid formation and its coalescence with the crack. This phenomenon accelerates the fatigue crack propagation. The degree of the strain-age hardening of carbon increases with increasing plastic strain, whereas the hydrogen-enhanced plastic strain localization at the crack tip can contribute to the increase in the degree of strain-age hardening at a ultra-low frequency ($1 \times 10^{-3}$ Hz), as long as the plastic strain localization does not cause microvoid formation prior to carbon segregation. The fatigue crack growth rate in hydrogen at $1 \times 10^{-3}$ Hz was lower in certain cases than that in nitrogen, as shown in Fig. 4. Strain-age hardening that was enhanced by the HELP effect could explain the partial deceleration of the fatigue crack growth at a test frequency of 6 Hz. However, the fatigue crack growth rate in the hydrogen atmosphere decreased with a drop in the frequency, and finally the acceleration effect of hydrogen on fatigue crack growth disappeared at a frequency of $1 \times 10^{-3}$ Hz when compared to the tests performed in the nitrogen atmosphere. We suggested that the disappearance of the acceleration effect of hydrogen on fatigue crack growth was caused by 1) the changing hydrogen distribution at the crack tip and 2) strain-age hardening caused by the presence of carbon. The fact that the fatigue crack growth rates in H$_2$ and N$_2$ were nearly equal at ultra-low frequencies indicates the availability of carbon steels in hydrogen gas atmospheres at specific frequencies.

4. Conclusions

In this study, we investigated the frequency dependence of the fatigue crack growth rate of an annealed low carbon steel (JIS S10C) with a ferrite/pearlite microstructure in hydrogen and nitrogen gas atmospheres. In the nitrogen atmosphere, the fatigue crack growth rate increased with decreasing frequency. In addition, the presence of hydrogen accelerated fatigue crack growth at a test frequency of 6 Hz. However, the fatigue crack growth rate in the hydrogen atmosphere decreased with a drop in the frequency, and finally the acceleration effect of hydrogen on fatigue crack growth disappeared at a frequency of $1 \times 10^{-3}$ Hz when compared to the tests performed in the nitrogen atmosphere. We suggested that the disappearance of the acceleration effect of hydrogen on fatigue crack growth was caused by 1) the changing hydrogen distribution at the crack tip and 2) strain-age hardening caused by the presence of carbon. The fact that the fatigue crack growth rates in H$_2$ and N$_2$ were nearly equal at ultra-low frequencies indicates the availability of carbon steels in hydrogen gas atmospheres at specific frequencies.

REFERENCES