Microscopic study on the effect of hydrogen on fatigue crack growth process in a chromium-molybdenum steel

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1. Introduction

In order to establish the safe use of hydrogen energy, it is of urgent necessity to clarify the effects of hydrogen on mechanical properties of structural materials. Typical metallic materials for structural use are ferrous-alloys such as chromium-molybdenum (chromoly) steel. Due to its high strength and durability, chromoly steel has been used for various structures that are subjected to harsh load conditions as in pressure vessels. Its application to structural bodies which are exposed directly to gaseous hydrogen is, on the other hand, yet to be generally accepted because the effect of gaseous hydrogen on the subcritical-crack growth property and the microscopic mechanism is not undersood well.

A number of studies have shown that high-strength steels charged with hydrogen exhibit significant susceptibility to hydrogen embrittlement. These studies have paid much attention to verifying the deleterious effect of hydrogen on macroscopic quantities such as loss of ductility, loss of fracture toughness or increase of crack growth rate. However, the dominant microscopic mechanism controlling the crack growth rate under hydrogen environment has not been extensively investigated except for limited studies based primarily on fractographic approach [1,2].

The objective of this study is to first investigate the effect of gaseous hydrogen on the fatigue crack propagation property of high-strength steel. Particular attention is paid on to JIS SCM435 chromoly steel, which is one of the candidate materials for pressure vessels used in hydrogen stations. Then the microscopic process of fatigue crack propagation is discussed in detail not only through a usual fractographic observation but also through a cross-sectional observation of the crack tip region by transmission electron microscopy (TEM).

2. Experiment method

The material used is a commercial chromium-molybdenum steel (JIS SCM435) whose chemical composition is tabulated in Table 1. The as-received material is first austenized at 1133 K for 9 ks and quenched in an oil bath to obtain martensite microstructure. Then the material is tempered at 743 K for 7.2 ks and cooled in air. The yield strength of the material is measured to be 1.25 GPa.

Table 1 Chemical composition of JIS SCM435 steel

Elements	C	Cr	Mo	Si	Mn	Ni	Cu	P	S	Fe
Wt%	0.38	1.11	0.15	0.22	0.84	0.08	0.12	0.02	0.02	Bal.

Fig. 1 illustrates the specimen geometry. The center of a round bar is machined to a smooth plate and a through-notch is introduced at the center position. The center-cracked tension (CCT) type specimen is uniaxially loaded in the longitudinal direction.

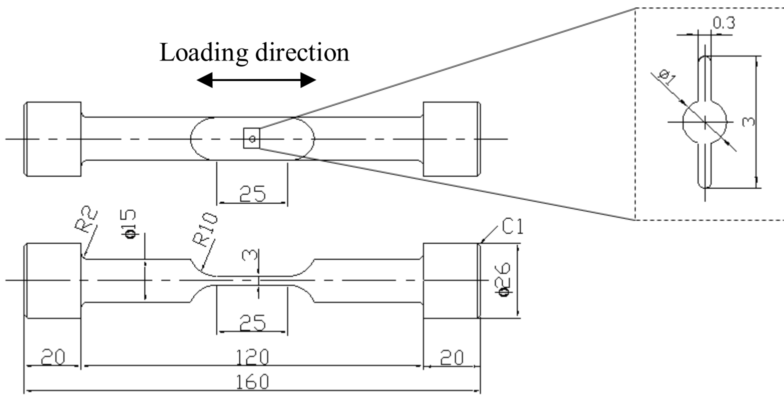

Fig. 1 specimen geometry.

The fatigue crack propagation test is conducted using a servo-hydraulic testing machine equipped with a gas chamber. The nominal stress is controlled to be 350 MPa with stress ratio of 0.05, and the stress wave form is sinusoidal with frequency of 1 Hz. In order to clarify the effect of gaseous hydrogen on the crack propagation property, another type of gas, i.e. helium (He) which is chemically inert, is also chosen as the reference. The purity of the gases are 99.999% and 99.995% for hydrogen and helium, respectively. The gas pressure (gauge value) of each atmosphere is kept constant at 0.58 MPa. The fatigue crack length is optically observed through a window of the gas chamber by a CCD camera. The test conditions are summarized in Table 2.

Table 2 Test conditions

Nominal maximum stress	Stress ratio	Wave form	Frequency	Atmosphere	
350 MPa	0.05	Sinusoidal	1 Hz	Hydrogen	0.58 MPa
				Helium	0.58 MPa

The tests are performed in two steps. First, the relationship between stress intensity factor range (ΔK) and crack propagation rate (da/dN) is preliminarily evaluated in helium and hydrogen atmosphere. ΔK value is evaluated by the following equation[3].

$$\Delta K = \Delta\sigma\sqrt{\pi a \sec\frac{\pi a}{2W}} \tag{1}$$

Here, $\Delta\sigma$ is the applied stress range, a is the crack half-length, W is the specimen half-width. Next, the crack propagation is interrupted at a certain ΔK value that yields different da/dN in each atmosphere (ΔK = 35 MPam$^{1/2}$ in this study). This allows a comparison of the different crack tip phenomenon at the same crack driving force.

After the fatigue crack propagation test, the crack surface and the crack tip region are carefully observed by scanning electron microscopy (SEM) and TEM respectively. For TEM observation, the terminated crack tip region is cut from the center thickness of the specimen and thinned by focused ion beam (FIB) process. The TEM observation is conducted using JEM-1300NEF (HVEM Lab. in Kyushu University) at ultra-high acceleration voltage of 1250 kV.

3. Results and discussion

Fig. 2 shows the relationship between the number of load cycles, N, and observed crack half-length, a, in helium and hydrogen atmosphere. The life before fatigue crack initiation from the notch root is much shorter in hydrogen than in helium. In addition, the fatigue crack propagates quite rapidly in hydrogen once it is initiated.

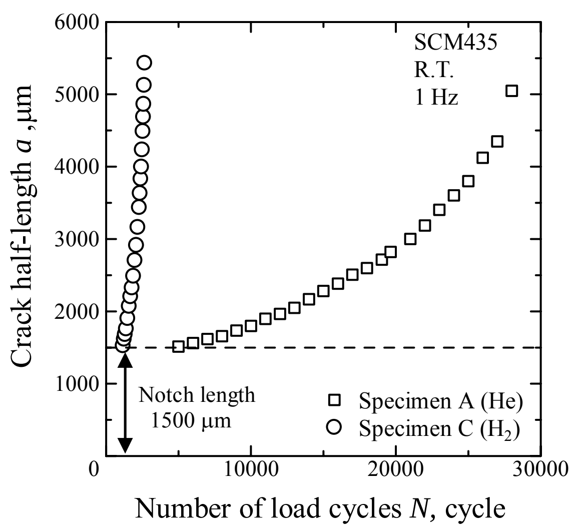

Fig. 2 Relationship between number of load cycles and crack half-length.

Fig. 3 shows the da/dN-ΔK relationships (stage IIb region) in helium and hydrogen atmosphere. It is evident that da/dN in Specimen C and D in hydrogen is remarkably larger compared to that in Specimen A and B in helium. Linear regression of the each plot (Specimen A, C) is implemented using the following Paris' formula.

$$\frac{\mathrm{d}a}{\mathrm{d}N} = C(\Delta K)^m \qquad (2)$$

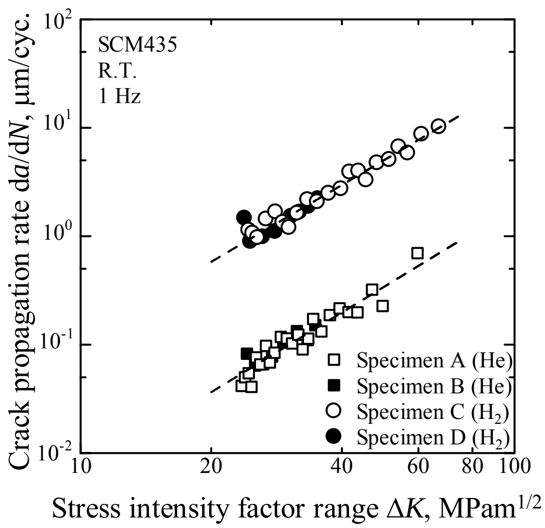

Fig. 3 Relationship between stress intensity factor range and crack propagation rate.

Table 3 Values of constants C and m

Specimen	C	m
A (in helium)	2.45×10^{-5}	2.44
C (in hydrogen)	5.03×10^{-4}	2.35

The constants C and m are derived as shown in Table 3. The m values here are relatively close to those reported for other high-strength steels (Cr-Mo [4] or Ni-Mo-V [5]) and relatively insensitive to the type of gas. It should be noted that the magnitude of da/dN in hydrogen atmosphere is about an order larger than in helium atmosphere.

Fig. 4 shows the fatigue crack surface of Specimen A observed by SEM. The general profile of the surface in low magnification is undulated due primarily to the original grain and/or sub-grain structure (packet, block) of martensite. The high magnification image of the surface shows the trace of ductile deformation. The spacing of the striation pattern is about 0.14 μm which is close to the measured da/dN value of 0.15 μm/cycle. The cross-sectional TEM image of the fatigue crack tip in Specimen B is shown in Fig. 5. Fine laths which are aligned in horizontal direction can be seen. The crack path is almost parallel to one group of laths. The magnified view of the crack reveals that the close vicinity of the crack surface is severely deformed. Particularly, the region specified by the dotted circle shows the wavy outline of the crack surface corresponding to the striation pattern observed in Fig. 4. These microscopic observations confirm that the fatigue crack propagation in helium atmosphere is essentially transgranular and dominated mainly by plastic process.

Fig. 6 shows the fatigue crack surface of Specimen C. The morphology of the crack surface is apparently different from that shown in Fig. 4; the general

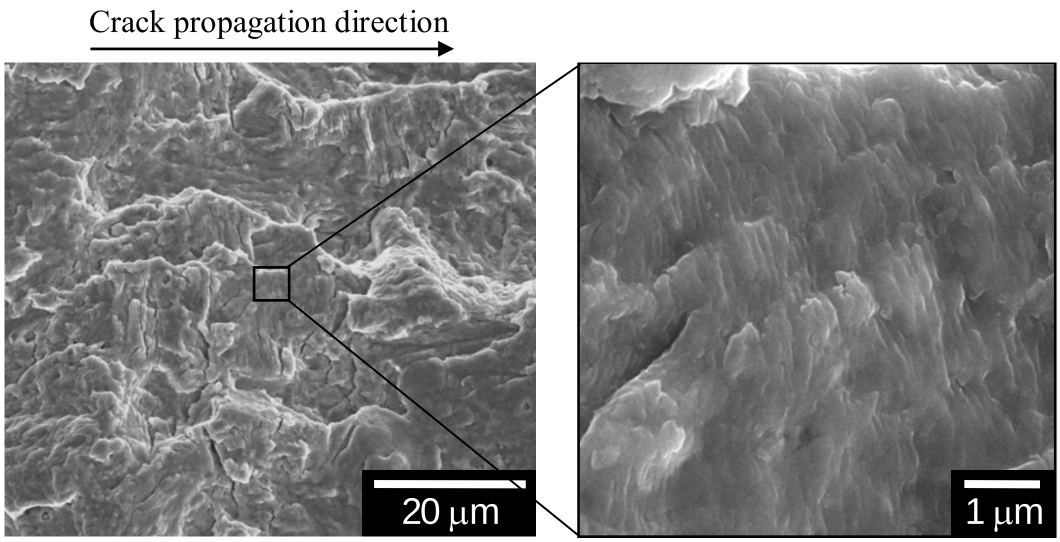

Fig. 4 SEM images of fatigue crack surface in helium (Specimen A, ΔK = 35 MPam$^{1/2}$, da/dN = 0.15 μm/cyc.).

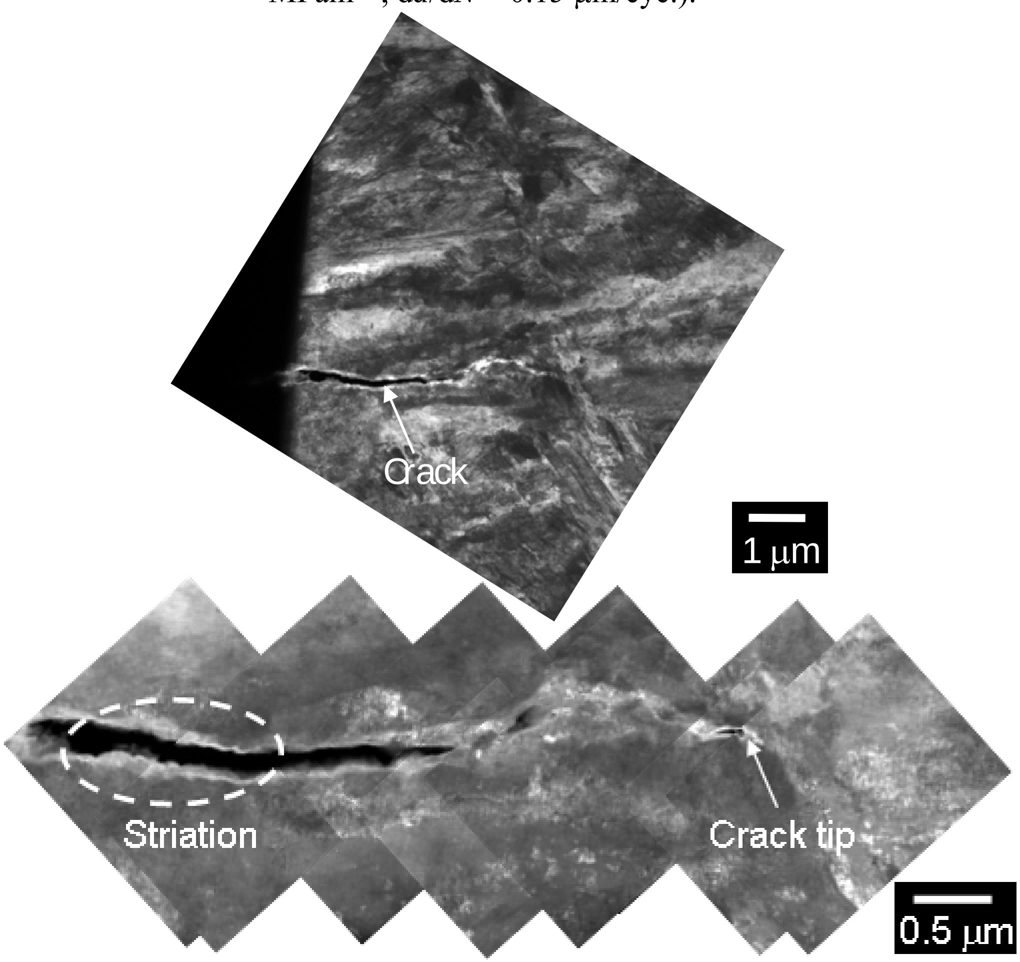

Fig. 5 Cross sectional TEM images of fatigue crack tip in helium (Specimen B, ΔK = 35 MPam$^{1/2}$, da/dN = 0.15 μm/cyc.).

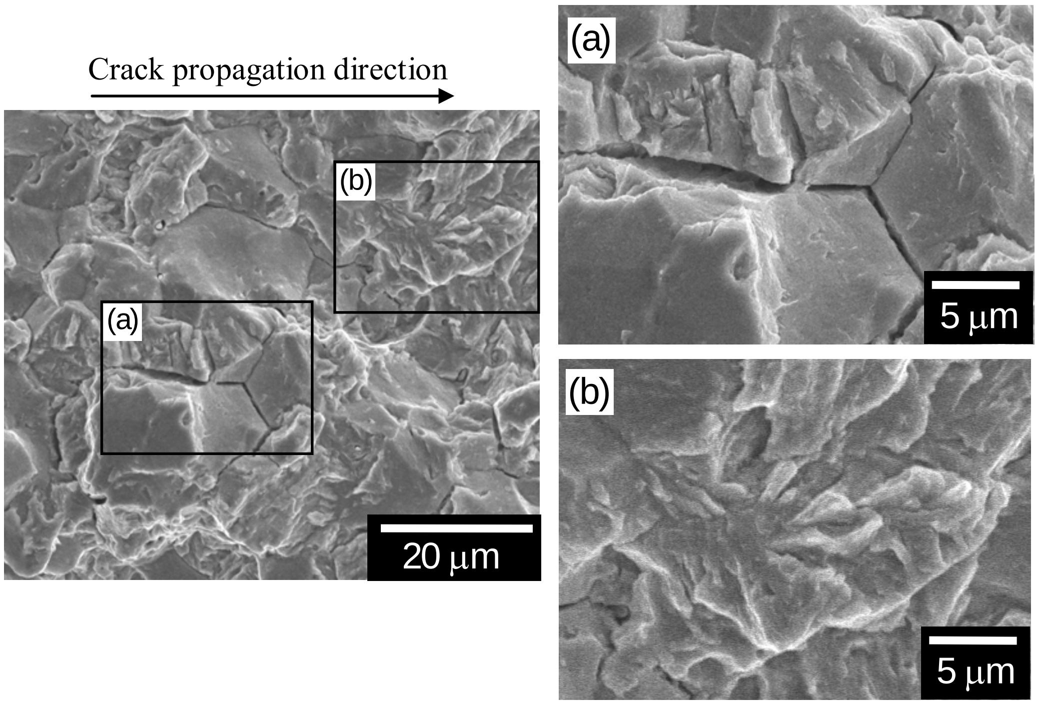

Fig. 6 SEM images of fatigue crack surface in hydrogen (Specimen C, ΔK = 35 MPam$^{1/2}$, da/dN = 2.2 μm/cyc.).

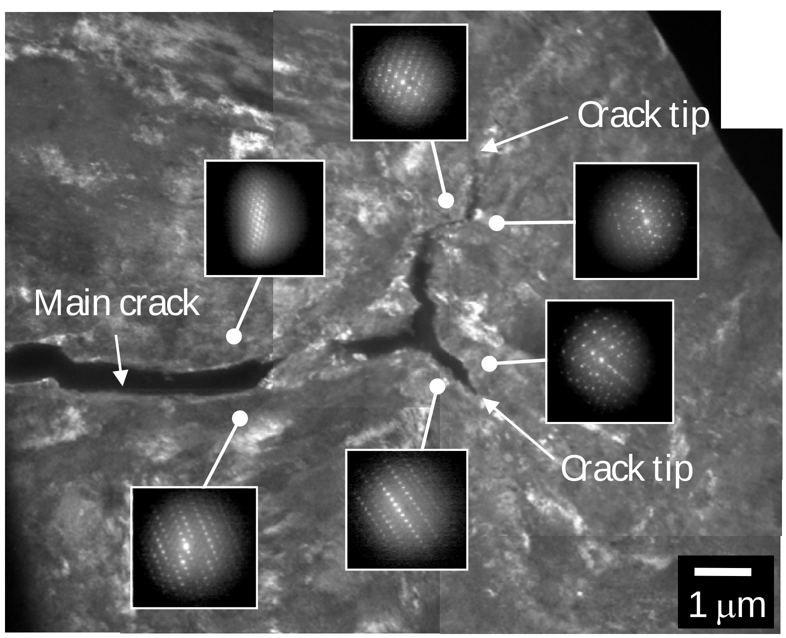

Fig. 7 Cross sectional TEM image of fatigue crack tip in hydrogen (Specimen D, ΔK = 35 MPam$^{1/2}$, da/dN = 2.2 μm/cyc.).

appearance is quite brittle in nature. Smooth facets of the original grain can be seen as shown in (a). The fine fragmented flat faces shown in (b) are formed as the result of quasi-cleavage fracture of sub-grain structure. The existence of crevices around facets indicates that the crack is likely to branch (or deviate) along grain boundaries. A clear evidence of the crack branching is also observed in the near-tip region of Specimen D as shown in Fig. 7. In Fig 7, the outline of the upper and lower crack surface mate well with each other. In addition, the crystallographic orientation of each region severed by the crack path is different from each other as shown by the electron diffraction patterns in the figure. These results indicate that, in hydrogen atmosphere, the fatigue crack preferably propagates along interface of grain and/or sub-grain in brittle manner [2, 4, 5] and could frequently be arrested by branching.

From the results of these microscopic observations, it can be postulated that the significant difference of da/dN in helium and hydrogen atmosphere is attributed to the difference in the physical mechanism of crack growth. In helium atmosphere, the magnitude of da/dN is determined mainly by the cyclic plastic deformation (blunting/re-sharpening) of the crack tip [6], which is usually found in ductile materials. In hydrogen atmosphere, on the other hand, the crack presumably propagates along grain and/or sub-grain interfaces in a brittle manner; it unstably propagates a distance comparable to the size of a unit interface until it encounters an arrester that enforces it to branch or deviate from the original path. This microscopic elementary process is randomly repeated along the crack front line and eventually determines the 'apparent' macroscopic crack growth rate, da/dN, with relatively large magnitude. Since the crack tip slip in SCM435 is originally constrained by the fine microstructures of martensite, the effect of hydrogen on the crack tip slip is expected to be rather small compared to the case of a non-martensite steel (e.g. JIS S10C [7]). An explicit observation of the dislocation structure near the crack tip would afford a better understanding of the growth mechanism, which is the objective of a future investigation.

4. Summary

The effect of hydrogen atmosphere on the fatigue crack propagation property of JIS SCM435 chromium-molybdenum steel is investigated. The magnitude of fatigue crack propagation rate, da/dN, is significantly larger in hydrogen atmosphere than in helium atmosphere. The fracture surface and the near-tip cross-section are observed in detail by SEM and TEM respectively. The microscopic observations suggest that the fatigue crack propagation in helium is transgranular and dominated by plastic process. On the other hand, the fatigue crack propagation in hydrogen is brittle cracking along interface of grain and/or sub-grain structures. The crack seems to advance by unstable growth accompanied frequently by branching or deviation, which eventually results in the relatively large growth rate.

Acknowledgments

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