EFFECTS OF HYDROGEN ON FATIGUE CRACK GROWTH BEHAVIOUR AND DUCTILITY LOSS OF AUSTENITIC STAINLESS STEELS

Toshihiko KANEZAKI*, Yoji MINE**
Yoshihiro FUKUSHIMA**, and Yukitaka MURAKAMI**
* Graduate School of Engineering, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
** Department of Mechanical Engineering Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
e-mail: ymura@mech.kyushu-u.ac.jp

Abstract

Effects of hydrogen on fatigue crack growth behaviour and ductility after fatigue cycles of austenitic stainless steels were investigated. In the hydrogen-charged specimens, the crack growth rates were approximately twice higher than those of the uncharged specimens for crack growth with the surface crack length $2a$ from 100 μm to 1000 μm. The aspect ratio for the crack with $2a = 1000$ μm was smaller in the hydrogen-charged specimens than in the uncharged specimens. Thus, due to high hydrogen content in surface layer, the crack growth rate in the surface layer was higher than that in the subsurface. Hydrogen charge decreased slip band density around the crack. It is known that ductility is reduced in tensile test carried out by interrupting fatigue test. However, there was a critical crack length for decrease in ductility. Hydrogen charge reduced the ductility by generating a large shear type crack produced by connection of small cracks that were nucleated on high hydrogen content surface.

Introduction

In the systems of fuel cell (FC), components such as liners of ultra-high pressure tanks and pipes are directly exposed to hydrogen. It has been reported that hydrogen degrades mechanical properties of metals significantly. There have been many studies on fracture and ductility of steels in hydrogen environment under static stress. It is known that reduction of area is intensively reduced in stainless steels subjected to tensile stress in high-pressure hydrogen environment [1]. This is presumed to arise from crack nucleation on the specimen surface by tensile stress and embrittlement at the crack tip [1, 2]. However, Murakami *et al* pointed out that the crack having a length longer than a critical value, L_c decreases the reduction of area in tensile test [3, 4]. In addition, in order to ensure safety and reliability of FC systems over the long term, it is most important to understand effects of hydrogen on fatigue behaviour. Austenitic stainless steels will be used for materials of FC components because of their high resistance to hydrogen intrusion. However, there have been few systematic studies on effects of hydrogen on fatigue strength in stainless steels. The objective of the present study is to clarify the influences of hydrogen on crack growth and loss of ductility.

Experimental Procedure

The materials used in this study were round bars made of a type 304 stainless steel (SUS304) and a type 316 stainless steel (SUS316). Table 1 shows the chemical compositions of the

materials. The round bars of SUS304 and SUS316 were solution-heat-treated at 1323 K and 1353 K, respectively. Subsequently, the round bars were machined to fatigue specimens. The Vickers hardness of SUS304 and SUS316 was H_v = 176 and 161, respectively.

Figures 1 (a) and (b) show the shape and dimension of tension-compression fatigue test specimen and artificial hole, respectively. The specimen surface was finished with buff after polishing by emery paper #2000. A small artificial hole with a diameter of 100 μm and a depth of 100 μm was drilled onto the specimen surface to limit the crack initiation sites and the number of cracks. In the hydrogen-charged specimens, the specimen surface was polished with buff after hydrogen charge, then the hole was introduced immediately. Charging hydrogen into specimens was performed by cathodic charge with platinum electrode at a current density of 2.3 mA/cm^2 in a pH = 3.5 aqueous solution of H_2SO_4 at 323 K for 672 hours. Fatigue tests were carried out at room temperature in laboratory air. The fatigue tests of the hydrogen-charged and uncharged specimens were conducted at a frequency of 1.2 Hz and 2 Hz, respectively, and at a stress ratio, R = -1, by tension-compression. Stress amplitude was controlled at 280 MPa for SUS304 and 260 MPa for SUS316. Crack growth behaviour was observed by the replica method. Tensile tests were conducted by interrupting fatigue test at a crosshead speed of 0.05 mm/s (approximately 2.5×10^{-3} /s in strain rate).

TABLE 1. Chemical compositions of materials (mass %).

	C	Si	Mn	P	S	Ni	Cr	Mo
SUS304	0.06	0.36	1.09	0.03	0.023	8.19	18.66	-
SUS316	0.05	0.27	1.31	0.03	0.028	10.15	17.01	2.08

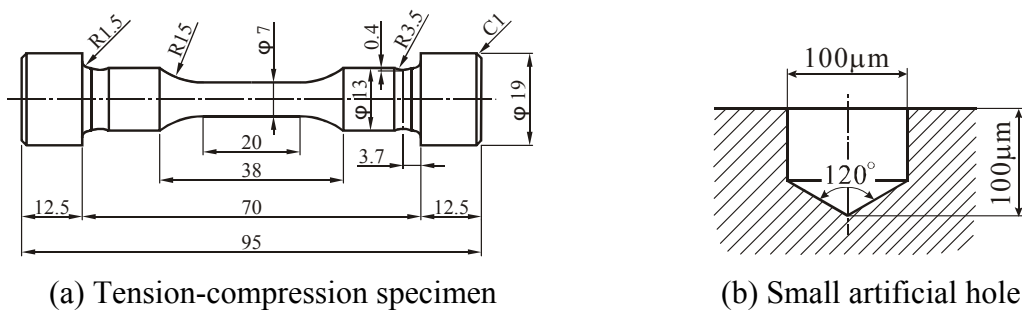(a) Tension-compression specimen   (b) Small artificial hole

FIGURE 1. The shape and dimension of specimen and artificial hole.

Experimental Results and Discussion

Hydrogen intrusion into specimens

It is known that hydrogen diffusion in austenitic stainless steels is remarkably slow compared with ferritic or martensitic stainless steels. The conditions of hydrogen intrusion into specimens were investigated to understand the distribution of hydrogen in the specimen. Figures 2 (a) and (b) show the hydrogen content distribution by using hydrogen-charged specimens of SUS304 and SUS316. In the specimen of SUS304, hydrogen was charged for 840 hours under the same conditions for fatigue test specimens. In the specimen of SUS316, hydrogen charge was performed by cathodic charge at a current density of 6.3 mA/cm^2 in a pH = 2.5 aqueous solution of H_2SO_4 at 323 K for 672 hours. After hydrogen charge, disks with thickness of 0.8 mm, which had different diameters by stepwise removing thin surface layer with emery paper, were cut off from the specimen. Hydrogen contents of the disks were

measured by thermal desorption spectrometry (TDS). The hydrogen content of the thin layer removed was calculated from the measurements. In the hydrogen-charged specimen, hydrogen content at approximately 200 μm in depth from the surface was the same as that in the uncharged specimen. These results indicate that hydrogen diffuses only into a very thin surface layer by hydrogen charge for 840 or 672 hours.
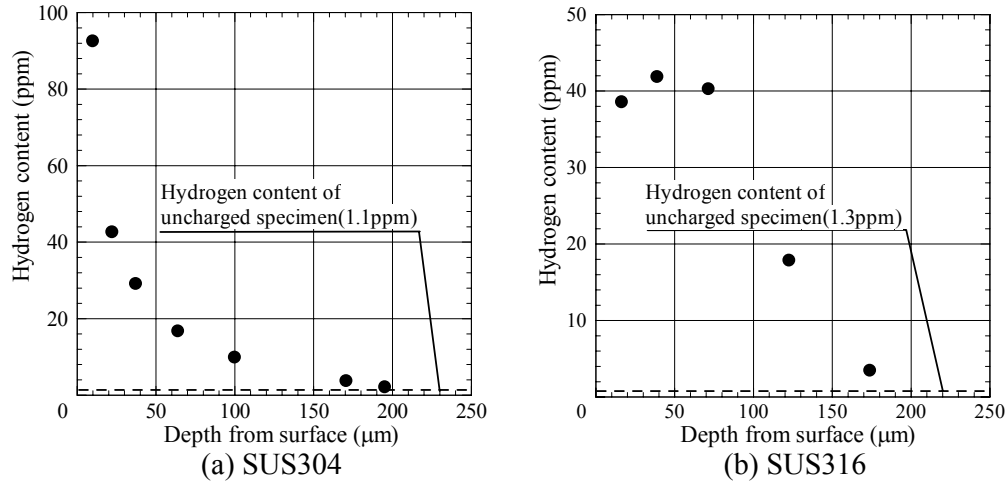

(a) SUS304   (b) SUS316

FIGURE 2. Hydrogen content distribution in hydrogen-charged SUS304 and SUS316.

Effects of Hydrogen on Fatigue Crack Growth Behaviour

Figures 3 (a) and (b) show the crack growth plots of SUS304 and SUS316, respectively. In the hydrogen-charged specimens, the crack growth rate, which was characterized by surface crack length $2a$ from 100 μm to 1000 μm, was approximately twice higher than that in the uncharged specimens. Table 2 shows the difference of the aspect ratio for the cracks between the hydrogen-charged specimens and the uncharged specimens. The aspect ratios for the cracks in the hydrogen-charged specimens were less than those in the uncharged specimens. Therefore, in the hydrogen-charged specimen, the crack growth rate with crack length $2a$ from 100 μm to 1000 μm was approximately 1.2 times higher in the surface layer than in the depth direction. The aspect ratio for the crack also decreased with increasing crack length in the hydrogen-charged specimen. Thus, higher hydrogen content in the surface layer accelerates the crack growth rate in the surface layer compared with the subsurface.

(a) SUS304 ($\sigma = 280$ MPa, $R = -1$)   (b) SUS316 ($\sigma = 260$ MPa, $R = -1$)
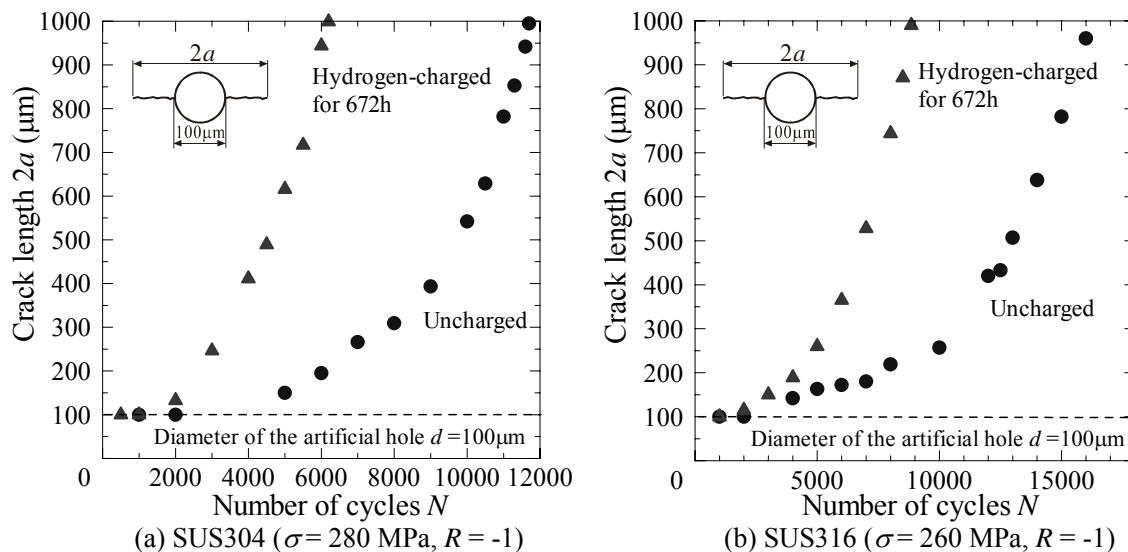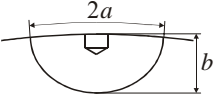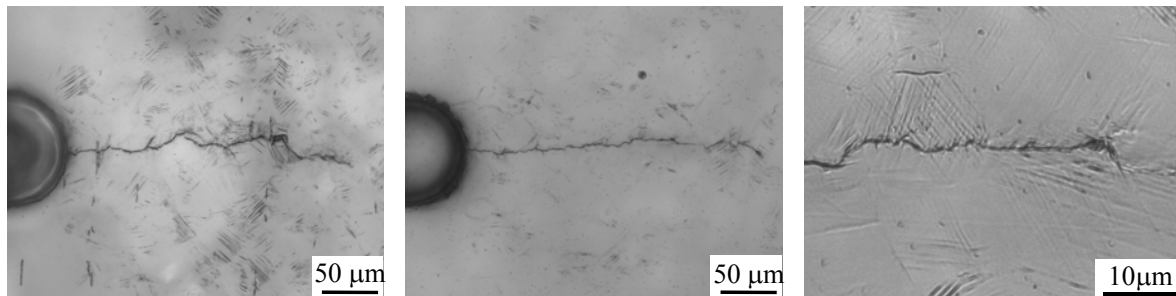
FIGURE 3. Influence of hydrogen on crack growth of SUS304 and SUS316.

Figures 4 (a)-(f) show the fatigue cracks emanating from the artificial hole in the uncharged and hydrogen-charged specimens of SU304 and SUS316. Slip band density around the crack in the hydrogen-charged specimens was less than that in the uncharged specimens. In particular, slip bands were localised in the vicinity of the crack tip in the hydrogen-charged specimens. This result is similar to the case observed in a medium carbon steel [5]. Although the crack growth path was zigzag in the uncharged specimens, it was relatively linear in the hydrogen-charged specimens. These results imply that the linear crack growth path in the specimen with hydrogen charge is caused not by embrittlement of material but by localisation of slips at the crack tip (see Figs. 4 (e) and (f)).
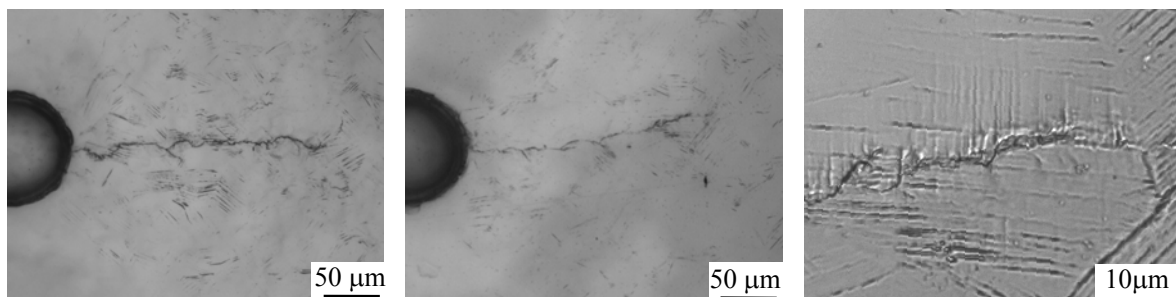
TABLE 2. The aspect ratios b/a for cracks.

	Crack length $2a$	Aspect ratio b/a of uncharged specimen	Aspect ratio b/a of hydrogen-charged specimen
SUS304	1000 μm	0.82	0.70
	1500 μm	0.82	0.61
SUS316	1000 μm	0.82	0.68

(a) Uncharged specimen of SUS304 ($\sigma = 280$ MPa, $N = 10500$)

(b) Hydrogen-charged specimen of SUS304 ($\sigma = 280$ MPa, $N = 5500$)

(c) Magnification of (b)

(d) Uncharged specimen of SUS316 ($\sigma = 260$ MPa, $N = 14000$)

(e) Hydrogen-charged specimen of SUS316 ($\sigma = 260$ MPa, $N = 7000$)

(f) Magnification of (e)

FIGURE 4. Cracks emanating from an artificial hole of the uncharged and hydrogen-charged specimens of SUS304 and SUS316.

Figure 5 shows SEM observations of fatigue fracture surfaces. Figure 6 shows the magnifications of the marked areas in Fig. 5. Clear striations were observed on the fatigue fracture surfaces of the uncharged specimens of SUS304 (Fig.6 (a)) and SUS316 (Fig.6 (c)). Although striations could be also observed in the hydrogen-charged SUS316 (Fig.6 (d)), clear striations were not observed in the hydrogen-charged SUS304 (Fig.6 (b)).
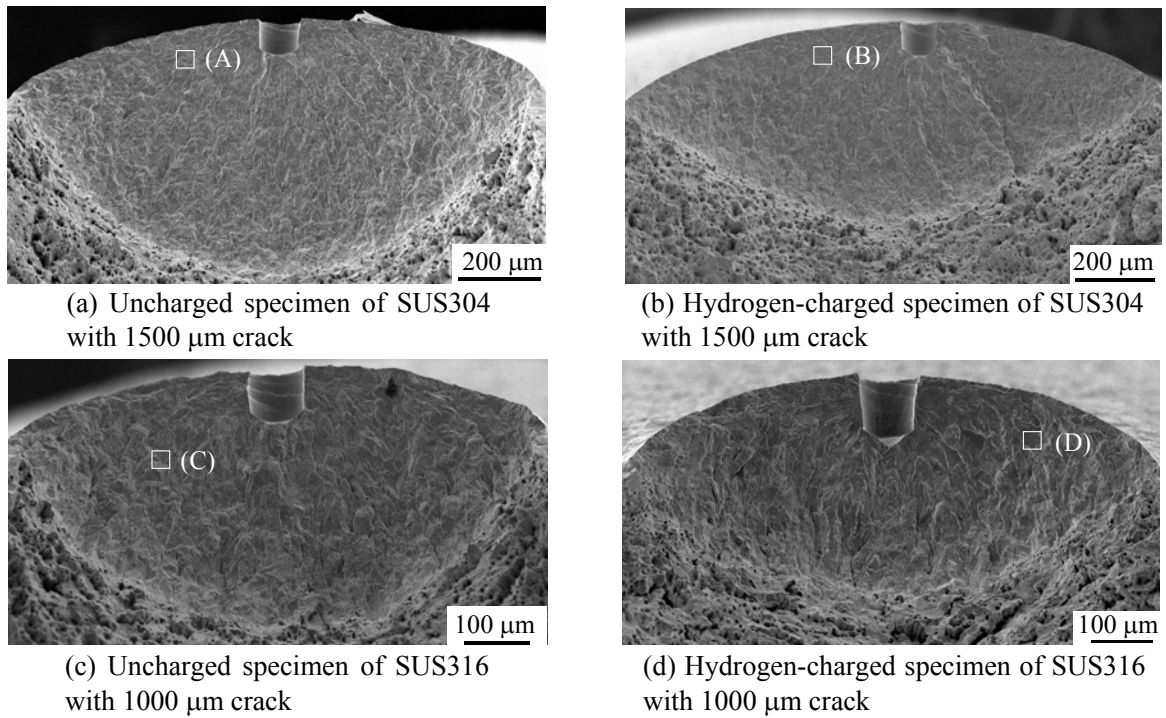
(a) Uncharged specimen of SUS304
with 1500 μm crack

(b) Hydrogen-charged specimen of SUS304
with 1500 μm crack

(c) Uncharged specimen of SUS316
with 1000 μm crack

(d) Hydrogen-charged specimen of SUS316
with 1000 μm crack

FIGURE 5. SEM observations of fatigue fracture surfaces.

(a) (A) in FIGURE 5. (a), SUS304
without hydrogen charge

(b) (B) in FIGURE 5. (b), SUS304
with hydrogen charge

(c) (C) in FIGURE 5. (c), SUS316
without hydrogen charge
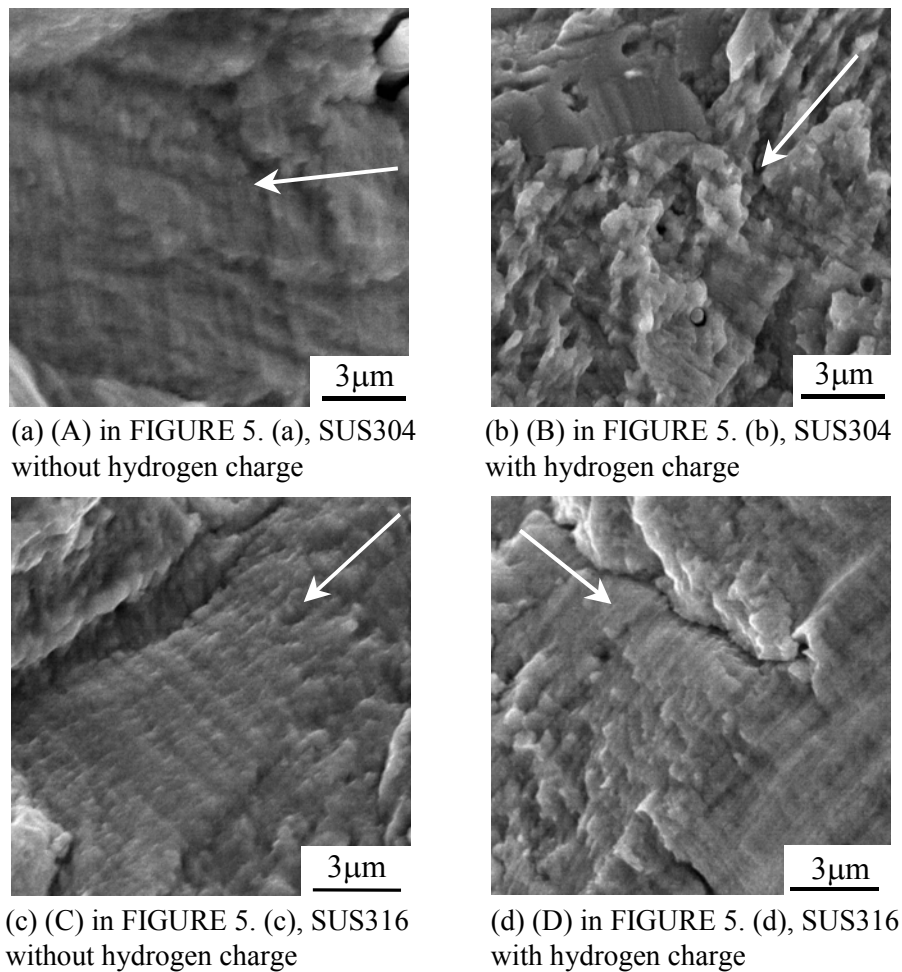
(d) (D) in FIGURE 5. (d), SUS316
with hydrogen charge

FIGURE 6. SEM observations of striations.
The arrows in the figures show the crack growth directions.

Effects of Hydrogen and Pre-crack on the Reduction of Area

A decrease in reduction of area (ductility) was obtained in tensile test carried out by interrupting fatigue test. Figure 7 shows the relationship between crack length and ductility loss. There is a critical crack length [3, 4], L_c for reduction of ductility: $L_c \approx 500$ μm for SUS304; $L_c \approx 700$ μm for SUS316.

In the uncharged specimens of SUS304 and SUS316, the similar fracture behaviour was observed. Figure 8 shows fracture appearances of the uncharged specimens with different pre-crack lengths of SUS304. The specimens with pre-crack length $L < L_c$, which did not affect ductility loss, essentially exhibited the so-called cup-and-corn type fracture as sown in Figs. 8 (a) and (b). In the uncharged specimens with 400 μm pre-crack, fracture did not originate from the pre-crack, and cup-and-corn type fractures were obtained at the minimum diameter sections as shown in Fig. 8 (b). This implies that the presence of the crack with $L < L_c$ does not influence the ductility loss. On the other hand, in the specimens with pre-crack length $L > L_c$, shear mode fractures by slips at the crack tip were observed (Fig. 8 (c) and (d)). Thus, the crack with $L > L_c$ causes a shear type fracture and decreases the ductility.

There were no definite differences in fracture morphology and ductility loss between the hydrogen-charged specimens and the uncharged specimens. However, hydrogen-charge into the specimens of SUS304 produced the connection of many small cracks that were nucleated on high hydrogen content surface resulting in a large shear type crack. Figure 9 shows fracture appearances of the hydrogen-charged specimens of SUS304. In the plain specimen with hydrogen charge, a shear type fracture partially appeared due to the cracks produced by tensile stress, which could be observed by the unaided eye (see Fig. 9 (a)). In the hydrogen-charged specimen with 1000 μm pre-crack, the shear type fracture was observed at the section of specimen other than the pre-crack as shown in Fig. 9 (c). Many cracks were observed on the surface near the fracture, and especially, at the crack tip. In the case of the hydrogen-charged specimen with 840 μm pre-crack, the shear type fracture started from the pre-crack and the ductility decreased more than that of uncharged specimen not only due to the pre-crack but also due to the cracks produced during tensile loading as shown in Fig. 9 (b). However, such cracks did not appear in the hydrogen-charged specimen with 1500 μm pre-crack, because the pre-crack was sufficiently large to grow alone in shear mode (see Fig. 9 (d)).
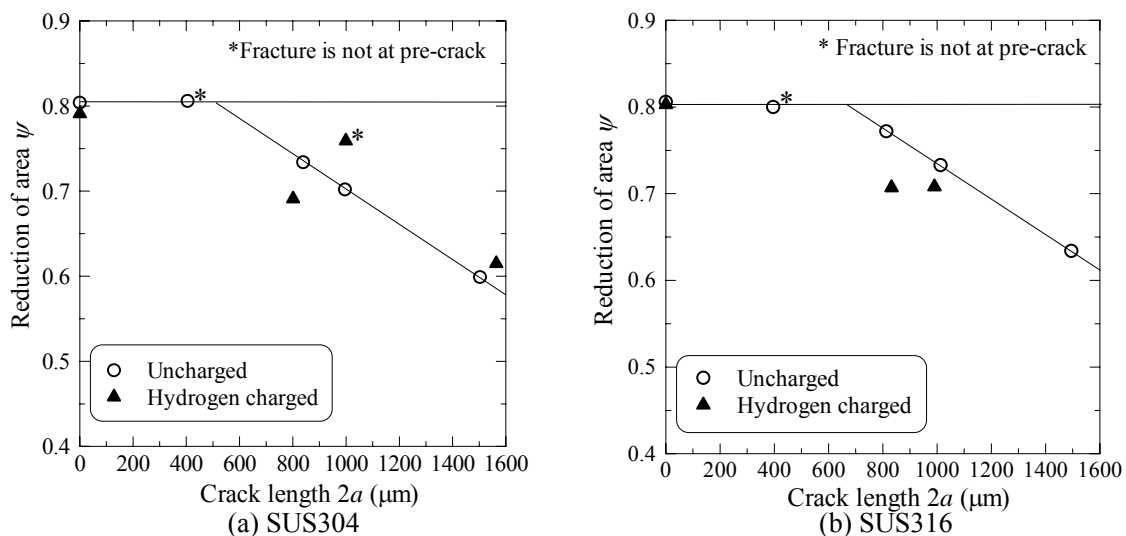

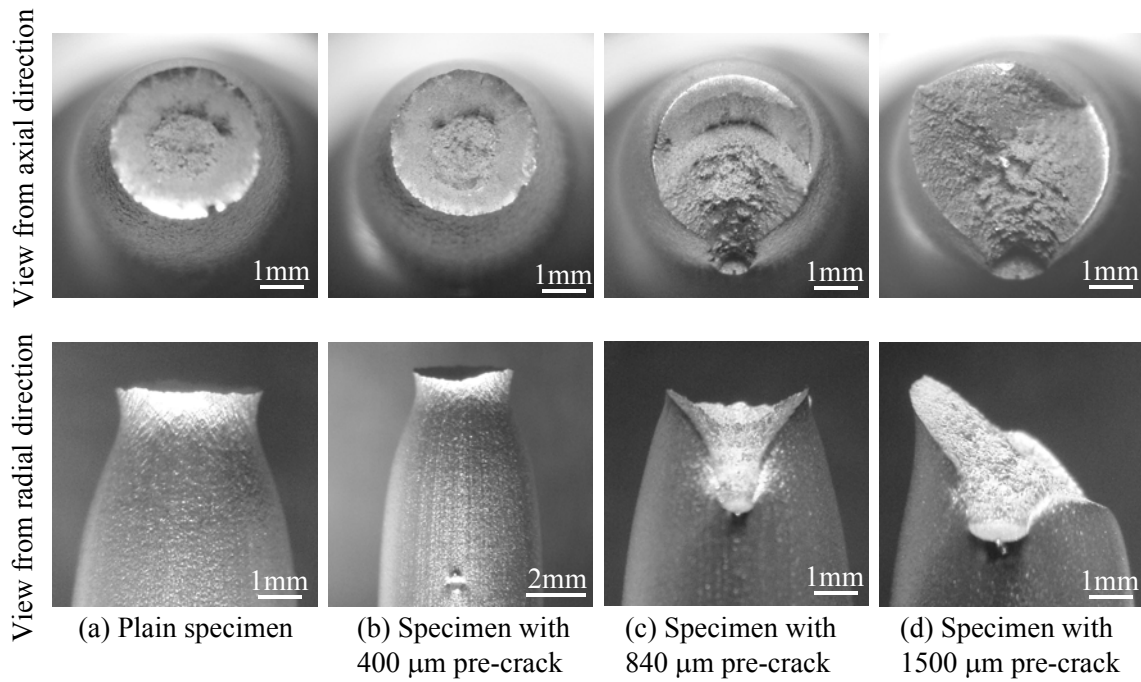FIGURE 7. Relationship between crack length and ductility loss.

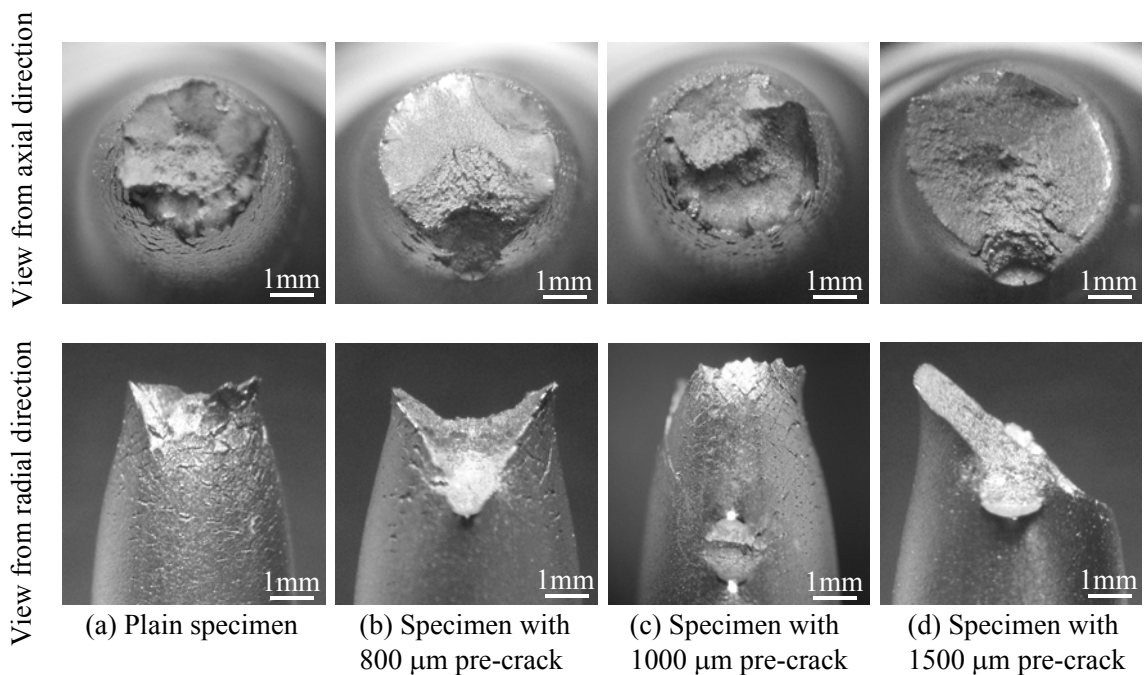FIGURE 8. Fracture observations of uncharged specimen of SUS304.

FIGURE 9. Fracture observations of hydrogen-charged specimen of SUS304.

The results obtained in the present study suggest that hydrogen causes coalescence of many small cracks, which were nucleated on high hydrogen content surface. However, there is no definite difference in ductility loss between the hydrogen-charged and uncharged specimens. On the other hand, Benson *et al* [1] reported ductility loss on stainless steels in tensile test in high-pressure hydrogen environment. This may be due to the difference in strain rate in two test conditions. In the present study, the tensile tests were conducted in air and the strain rate was ~ 2.5×10^{-3} /s. On the other hand, Benson *et al*'s test was conducted in high-pressure hydrogen at a slow strain rate of ~ 2.9×10^{-4} /s. In the condition of slow strain rates in high-pressure hydrogen environments, there is sufficient time for hydrogen diffusion

into material and many cracks initiate and grow during test until a main crack grows up to the critical length after coalescence. Thus, the ductility loss in the present study (strain rate $\sim 10^{-3}$ /s) is not directly caused by prior fatigue history or hydrogen embrittlement but depends on the crack length produced during fatigue cycles.

Conclusion

Effects of hydrogen on fatigue crack growth behaviour and ductility after fatigue cycles of austenitic stainless steels were investigated. The conclusions can be summarised as follows.

(1) In the hydrogen-charged specimens, the crack growth rate within the surface crack length $2a$ from 100 μm to 1000 μm was approximately twice higher than that in the uncharged specimens. In the hydrogen-charged specimens of SUS304 and SUS316, the aspect ratios were smaller than those in uncharged specimens. Thus, higher hydrogen content in surface layer accelerates the crack growth rate on surface layer compared with the subsurface.

(2) Slip band density around the crack in the hydrogen-charged specimens was less than that in the uncharged specimens. Although the crack growth path was zigzag in the uncharged specimens, it was relatively linear in the hydrogen-charged specimens.

(3) Clear striations were observed on fatigue fracture surface of SUS304 and SUS316 without hydrogen charge. Although striations could be also observed in the hydrogen-charged specimen of SUS316, clear striations were not observed in the hydrogen-charged specimen of SUS304.

(4) Reduction of area (ductility) in tensile test carried out by interrupting fatigue test decreased with fatigue cycles. There was a critical crack length for loss of ductility. In the present test, $L_c \approx 500$ μm for SUS304, $L_c \approx 700$ μm for SUS316.

(5) In hydrogen-charged specimens, hydrogen did not directly affect the ductility loss. However, hydrogen causes coalescence of many small cracks, which were nucleated on high hydrogen content surface. The ductility loss is not directly caused by prior fatigue history or hydrogen embrittlement but depends on the crack length produced during fatigue cycles of strain rate of $\sim 2.5 \times 10^{-3}$ /s.

Acknowledgments

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