Effect of hydrogen cathodic charging on fatigue fracture of type 310S stainless steel

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Abstract. It is known that hydrogen embrittlement occurs in austenitic stainless steels like type 304 because of the strain induced martensitic transformation. Rotary bending fatigue tests of type 310S stainless steel with hydrogen cathodic charging were carried out to investigate the effect of hydrogen charging on the austenitic phase. High dissolved hydrogen decreases the fatigue strength. It also enhances the plasticity and induces ε martensitic transformation. Hydrogen may promote crack initiation in slip bands.

1. Introduction
Austenitic stainless steels have been utilized as materials for equipments related to hydrogen energy lately, because they have high tolerance for hydrogen embrittlement. It is, however, known that hydrogen embrittlement occurs in type 304 because of stress induced martensitic transformation [1]. It was reported that hydrogen embrittlement does not occur in type 310S, which is most stable austenitic steel [1]. It is difficult to measure the effect of hydrogen on tensile tests of the bulk, because hydrogen diffusivity in 310S is quite small and the affected region is limited to the surface layer. Inoue et al. [2] reported that the elongation of a thin sheet decreases under high hydrogen fugacity and the crack propagation is influenced by hydrogen induced martensitic transformation.

It is considered that the effect of hydrogen on fatigue tests is remarkable compared with tensile test, because the interaction between hydrogen and slip bands plays an important role in hydrogen embrittlement. It is reported [3] that hydrogen induces micro cracks along slip bands and enhances the fatigue crack growth in 310S. However, the effect of hydrogen on the fatigue strength has not been clarified. Rotary bending tests were carried out up to high cycle region and X-ray diffraction was used to investigate the effect of hydrogen on the fatigue strength of 310S austenitic stainless steel in the present paper.

2. Experimental procedures
Specimens were machined from φ8mm drawing rods of type 310S stainless steel, whose chemical composition is shown in Table 1. Dimensions of the fatigue specimen are shown in figure 1. Its surface was polished chemically by the aqueous
solution that contains 2.9 mass% of hydrofluoric acid and 29 mass% of hydrogen peroxide after polishing mechanically by alumina powder (0.1 µm).

| Table 1. Chemical composition (mass%) |
|--------------------------------------|
| C   | Si  | Mn  | P   | Ni   | Cr   | S   |
| 0.02 | 0.3 | 1.07 | 0.028 | 19.26 | 24.1 | 0.001 |

Rotary bending fatigue tests were carried out using a water tank, as shown in figure 2, to charge hydrogen into a specimen. The tank was filled with an electrolytic solution that contained 0.5 kmol/m³ sulfuric acid and 1.4 kg/m³ thiourea. Cathode current was passed through the specimen during a fatigue test. The temperature of the solution was held at 300 K. A frequency of cyclic stress was 60 Hz.

For comparison, fatigue tests were also carried out in glycerin, which was used to keep a temperature 300 K under the hydrogen-free condition. Moreover, to free the surface reaction from the electrolytic solution, fatigue tests of hydrogen-precharged specimen were carried out in glycerin. The hydrogen pre-charge was run for 48 hours in the same electrolytic solution, in which the current density was 2590 A/m².

X-ray diffraction was employed with Cr Kα and Co Kα radiation to prove the existence of martensite phase and hydrides. In the measurement, an incident angle was fixed at 5 degree.

3. Results and discussion

3.1. Fatigue tests

S-N curves are shown in figure 3. The fatigue strength $\sigma_a$ with hydrogen charging up to a current density 490A/m² was almost the same as that in glycerin without hydrogen. In the condition whose current density is 2590A/m², the fatigue strength decreased slightly. The decrease in strength was also obtained on the fatigue tests of hydrogen-precharged specimen in glycerin. It takes almost 48 hours for a fatigue test up to $10^7$ cycles. It is considered that an amount of absorbed hydrogen is almost the same in the test with hydrogen charging and in glycerin after hydrogen pre-charged at high cycle if the hydrogen transport by dislocation is disregarded. This result implies that the fatigue strength is affected not by the surface reaction but by the dissolved hydrogen. Moreover, we confirmed that the fatigue strength deceased similarly, even if a specimen was polished by alumina powder after hydrogen pre-charging.
3.2. Fracture surfaces

A lot of traces of the slip bands were observed on the fracture surfaces, as shown in figure 4. The trace is almost straight on the fracture surface in glycerin (figure 4 (c)), while it is wavy on the fracture surfaces of specimens with hydrogen (figure 4 (a) (b)). This indicates that hydrogen enhances plastic deformation. There is no secondary crack on the fracture surfaces in glycerin, but there are many cracks with hydrogen. Such cracks were observed near the side surface, and hardly observed in the centre of specimens (figure 5). Moreover, cracks along slip bands were observed on the side surfaces of the specimens charged with hydrogen (figure 6). This corresponds to the observation of cracks by Mine et al. [3] The fracture surfaces of specimens with hydrogen charging and those tested in glycerin after hydrogen pre-charged are similar. This is in agreement with S-N curves.

Figure 4. Fracture surfaces near the side surface (a) with hydrogen charging ($i_c=2590\text{A/m}^2$, $\sigma_a=204\text{MPa}$, $N_f=1.9 \times 10^6$), (b) in glycerin after hydrogen pre-charged ($\sigma_a=163\text{MPa}$, $N_f=2.2 \times 10^6$) and (c) in glycerin without hydrogen ($\sigma_a=187\text{MPa}$, $N_f=6 \times 10^6$).

Figure 5. Fracture surfaces in the centre of the specimen (a) in glycerin without hydrogen ($\sigma_a=187\text{MPa}$, $N_f=6 \times 10^6$) and (b) with hydrogen charging ($i_c=2590\text{A/m}^2$, $\sigma_a=204\text{MPa}$, $N_f=1.9 \times 10^6$).

Figure 6. Side surfaces (a) with hydrogen charging ($i_c=2590\text{A/m}^2$, $\sigma_a=204\text{MPa}$, $N_f=1.9 \times 10^6$) and (b) in glycerin after hydrogen pre-charged ($\sigma_a=163\text{MPa}$, $N_f=2.2 \times 10^6$).
3.2 X-ray diffraction
No other phase except γ phase was detected on all fracture surfaces as shown in figure 7. That is, neither stress induced martensitic transformation nor hydride was detected. On the other hand, the martensite phase was detected on the surface of a specimen into which hydrogen was charged without stress (figure 8). It is not stress induced martensite ε but hydrogen induced εH. Kamachi [4] has presented that εH phase is transformed from γ phase when hydrogen is charged for long time. Any hydride was not detected on the surface as well as on the fracture surface. Then, it is considered that absorbed hydrogen did not induce hydrides but εH martensite phase and this phase disappeared during fracture process.

4. Discussion
High dissolved hydrogen may promote crack initiation in slip bands and decrease the fatigue strength. The effect of hydrogen on the crack initiation in slip bands is considered as follows. In the first, it is due to hydrogen-enhanced localised plasticity, which was observed on the fracture surface. In the second, it is brittle fracture of εH martensite induced by hydrogen, which was detected on the surface of hydrogen charged specimen without stress. In the third, it is hydrogen segregation in slip bands, which enhances the internal pressure. Polák et al. [5] proposed that the intrusions take an important role in fatigue crack initiation of stainless steel. The influence of hydrogen on fatigue fracture may be related to the mechanism. A further research is necessary which mechanism governs the fatigue behaviour of 310S in the hydrogen environment.

5. Conclusion
It is concluded that high dissolved hydrogen decreases the fatigue strength in type 310S stainless steel. Hydrogen may promote crack initiation in the slip bands under the cyclic stress condition. But, the mechanism of the crack initiation is under discussion.

References
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