Hydrogen embrittlement property of a 1700-MPa-class ultrahigh-strength tempered martensitic steel

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Abstract
The hydrogen embrittlement property of a prototype 1700-MPa-class ultrahigh-strength steel (NIMS17) containing hydrogen traps was evaluated using a slow strain rate test (SSRT) after cathodic hydrogen precharging, cyclic corrosion test (CCT) and atmospheric exposure. The hydrogen content in a fractured specimen was measured after SSRT by thermal desorption spectroscopy (TDS). The relationship between fracture stress and hydrogen content for the hydrogen-precharged specimens showed that the fracture stress of NIMS17 steel was higher, at a given hydrogen content, than that of conventional AISI 4135 steels with tensile strengths of 1300 and 1500 MPa. This suggests better resistance of NIMS17 steel to hydrogen embrittlement. However, hydrogen uptake to NIMS17 steel under CCT and atmospheric exposure decreased the fracture stress. This is because of the stronger hydrogen uptake to the steel containing hydrogen traps than to the AISI 4135 steels. Although NIMS17 steel has a higher strength level than AISI 4135 steel with a tensile strength of 1500 MPa, the decrease in fracture stress is similar between these steels.

Keywords: hydrogen embrittlement, delayed fracture, atmospheric corrosion, slow strain rate test, thermal desorption spectroscopy, high-strength steel

1. Introduction
High-strength steels are susceptible to hydrogen embrittlement [1] and the susceptibility increases with the strength level of steels above 1200 MPa [2]. Hydrogen embrittlement is a problem that confronts the development of high-strength steels. In the early 1980s, Pressouyre and Bernstein reported that a critical local concentration of hydrogen is required to cause embrittlement. They suggested taking advantage of good hydrogen traps with respect to their ability to either increase the time to reach the critical concentration or to disperse the hydrogen, so that the critical local concentration is not reached [3]. Hydrogen trapping is expected to improve the resistance of high-strength steels to hydrogen embrittlement, and the role of hydrogen-trapping materials such as VC [4] and TiC [5] has been studied.

Kimura et al [6] have developed a 1700-MPa-class ultrahigh-strength bolt from a prototype of low-alloy martensitic steel, Fe-(0.6C-2Si-1Cr-1Mo). This steel is labeled as NIMS17. To achieve the high strength of martensitic structure with resistance to hydrogen embrittlement, the
Table 1. Chemical composition (wt.%) at the prototype steel used in this study.

| C  | Si | Mn | P   | S   | Cr | Mo | Fe |
|----|----|----|-----|-----|----|----|----|
| 0.59 | 1.98 | 0.20 | < 0.002 | < 0.001 | 0.99 | 0.94 | 95.3 |

The relationship between the fracture stress and diffusible hydrogen content was evaluated using SSRT of hydrogen-precharged specimens. The measurement of hydrogen content is described in section 2.4. The specimens were charged with hydrogen by cathodic polarization in either a 3% NaCl + 0.3% NH₄SCN or a 0.1 N NaOH aqueous solution at a current density of 0.3–30 A m⁻² for 72 h. After the hydrogen charging, the specimens were mechanically polished with #1000 grit SiC paper and electroplated with cadmium to prevent hydrogen release during SSRT. SSRT was carried out for the hydrogen-precharged specimens using a Shimadzu AG-250kNI tensile machine with a constant crosshead speed of 0.005 mm min⁻¹ that corresponds to a nominal strain rate of 8.3 × 10⁻⁷ s⁻¹. The fracture stress, σf, was evaluated as σf = Fmax/Amin, where Fmax is the maximum tensile load and Amin is the initial cross-sectional area of the notch in the specimen. The stress monotonically increased with displacement during SSRT of a hydrogen-precharged specimen, and the maximum tensile stress was the same as the fracture stress; thus, SSRT took up to about 6 h. After fracture, the specimen was immediately immersed in liquid nitrogen and kept there to avoid hydrogen release. The cadmium plating was removed by anodic dissolution.

2.2. Slow strain rate test (SSRT) of hydrogen-precharged specimens and fracture surface observation

To investigate the effect of hydrogen uptake due to atmospheric corrosion on the mechanical properties of NIMS17 steel, the fracture stresses of notched bar specimens were measured using SSRT after CCT. The CCT condition is the same as in the previous study [15]. The CCT cycle lasted 8 h and included a dry step at 50% relative humidity (RH) for 5.75 h, a wet step at 98% RH for 1.75 h and a salt spray step using a 0.5 wt.% NaCl solution for 0.5 h. All the steps were carried out at 30 °C. After CCT, fracture stresses of the atmospherically corroded specimens were measured using SSRT. The specimens were covered with paper wetted with deionized water during SSRT to maintain the humidity of their surfaces and to support the corrosion and hydrogen uptake.

To investigate hydrogen uptake from the atmosphere, notched bar specimens were also exposed at two sites: in a rural area in Tsukuba and in a rural/coastal area in Choshi, Japan. The exposure tests in Tsukuba and Choshi were started on 5 February and 25 January 2007, respectively. The environmental factors at the exposure sites are shown in Table 2 [16]. The corrosion rate of a carbon steel is higher at Choshi [16] than at Tsukuba. Fracture stresses of the exposed specimens were measured using SSRT every three months, and the hydrogen content in the specimens was measured after SSRT. Prior to SSRT, the atmospherically corroded specimens retrieved from the exposure sites were kept at 98% RH at 30 °C for 24 h to introduce hydrogen by reproducing corrosion affected by the rust layers formed during exposure. This procedure also aimed to homogenize the hydrogen distribution [12]. During SSRT of the exposed...
Table 2. Environmental factors at exposure sites in Tsukuba and Choshi, Japan. The values are averaged over the period of 2002–2005 [16].

| Factor                                      | Tsukuba       | Choshi        |
|---------------------------------------------|---------------|---------------|
| Environment                                 | Rural         | Rural/coastal |
| Latitude (North) and longitude (East)       | 36°4', 140°7' | 35°43', 140°45' |
| Air temperature (°C)                        | 15.8          | 14.3          |
| Relative humidity (%)                       | 75            | 77            |
| Chloride deposition rate (mg NaCl m⁻² day⁻¹) | 2.2           | 36.0          |
| Corrosion rate (g m⁻² year⁻¹)² of carbon steel, SM490A | 141           | 252           |

*Calculation based on NIMS Corrosion data sheet No.3 A [16].

Figure 2. Typical hydrogen desorption spectrum of a hydrogen-charged NIMS17 steel specimen.

specimens, their surfaces were kept wet by covering with wet paper. Other SSRT conditions are the same as those for SSRT of hydrogen-precharged specimens as described earlier. The fracture surfaces were cut off from the fractured specimens and observed by scanning electron microscopy (SEM).

2.4. Thermal desorption spectroscopy (TDS)

The hydrogen content in specimens after SSRT was measured using a TDS apparatus (R-Dec Co Ltd), which is equipped with a programmable furnace and a quadrupole mass spectrometer. The heating rate was 100 °C h⁻¹. Figure 2 shows a typical hydrogen desorption spectrum of a specimen charged with hydrogen electrochemically in NaOH aqueous solution at 1.5 A/m² for 72 h. The spectrum of a specimen without hydrogen charging is also shown for comparison. The total desorbed hydrogen corresponding to the first peak appearing up to about 300 °C was considered as diffusible hydrogen [15] introduced in the specimen. The integrated hydrogen desorption rate from room temperature to 300 °C (about 100000 s) was normalized by the specimen’s weight and the resulting value was defined as diffusible hydrogen content, H_D. For the measurement of hydrogen content in specimens after CCT and atmospheric exposure, the rust layer formed on the specimen was removed using a sand blaster before TDS.

Figure 3. Relationships between fracture stress and diffusible hydrogen content, H_D, for NIMS17 and AISI 4135 steels.

3. Results and discussion

3.1. Relationship between fracture stress and hydrogen content

Figure 3 shows the relationship between the fracture stress and hydrogen content for hydrogen-charged NIMS17 steel specimens. The corresponding values for AISI 4135 steels with tensile strengths of 1300 and 1500 MPa, represented as B13 and B15, respectively, are also shown for comparison [13, 14]. The fracture stress decreases with increasing hydrogen content. Among these steels, NIMS17 steel shows the highest fracture stress at a given hydrogen content. This indicates that NIMS17 steel, despite its highest strength level, is less susceptible to delayed fracture as determined from hydrogen-content-based evaluation. This is probably because hydrogen trap sites of nanoscale carbides increase the diffusible hydrogen content for hydrogen embrittlement fracture [6, 8] and because of the structure resistance to hydrogen embrittlement. Figure 3 also shows H_C obtained using the constant load test [7] with an applied load of 0.9 tensile strength [6, 8]. The value is in a good agreement with the curve obtained using SSRT.

3.2. Relationship between fracture stress and H_E of NIMS17 steel corroded during CCT

Figure 4 shows the relationship between the fracture stress and content of hydrogen originating from the environment,
Fracture stresses and diffusible hydrogen contents, $H_E$, of the specimens corroded during CCT. The result for AISI 4135 steel with a tensile strength of 1500 MPa (B15) obtained using SSRT at 98% RH is also shown for comparison [15]. The hydrogen content of NIMS17 steel increases with the CCT cycle number and the fracture stress decreases correspondingly until about 90 cycles of CCT. A correspondence between them is also observed at a later stage of CCT when the hydrogen content decreases and fracture stress recovers. A similar recovery of fracture stress is observed for B15 steel, although $H_E$ does not decrease when the fracture stress recovers. This is probably because $K_t$ decreased as a result of the increase in notch root radius following corrosion [15].

The lowest fracture stress of NIMS17 steel is about half of its notch tensile strength without hydrogen uptake. The maximum $H_E$ for NIMS17 steel is about 0.6 wt ppm, which is clearly higher than that of B15 steel. This can be attributed to the hydrogen traps in NIMS17 steel. The maximum $H_E$ of the NIMS17 steel specimen is higher than the $H_C$. Therefore, NIMS17 steel is susceptible to hydrogen embrittlement under this accelerated corrosion condition. Hydrogen trapping effect is expected by some researchers to mitigate hydrogen embrittlement by reducing the local hydrogen concentration at crack initiation sites. However, when hydrogen intrusion is continuous in such a severely corrosive environment, the added hydrogen trap may increase the total hydrogen uptake but may not decrease the concentration of free hydrogen that causes fracture. Under the CCT condition in this study, the expected effect of hydrogen trap to mitigate hydrogen embrittlement was not evident.

Even if NIMS17 steel has a higher tensile strength than B15 steel, the decrease in fracture stress of NIMS17 steel is similar to that of B15 steel. This implies improved resistance of NIMS17 steel to hydrogen embrittlement.

### 3.3. Relationship between fracture stress and $H_E$ of NIMS17 corroded during outdoor exposure

Figures 5 and 6 show the change in fracture stress and hydrogen content in NIMS17 steel with exposure time. Although there is no data from the Choshi exposure site after 9 months, there is a clear difference between the exposure sites in terms of both the fracture stress and hydrogen content. The rural/coastal environment of Choshi is more corrosive than the rural environment of Tsukuba because of the higher chloride deposition rate (table 2). This is presumably responsible for the higher diffusible hydrogen content in the specimens exposed at Choshi; their lower fracture stress can be attributed to the higher hydrogen content. The change in the fracture stress with exposure time also corresponds to the change in the hydrogen content.
Figure 7. SEM fractographs of NIMS17 steel specimens with diffusible hydrogen content, $H_D = 0$ (a), $H_D = 0.54$ wt ppm (b), $H_D = 1.0$ wt ppm (c) and $H_D = 3.7$ wt ppm (d).

Figure 8. SEM fractographs of NIMS17 steel specimens exposed at Choshi for 3 months ($H_E = 0.15$ wt ppm, $\sigma_f = 1500$ MPa).

The corrosive environments at both exposure sites are less aggressive than the CCT environment in this study. Nevertheless, the fracture stress clearly decreased for NIMS17 steel exposed either at Choshi or at Tsukuba. Accordingly, it is predicted that bolts made of steel whose maximum stress concentration factor is as high as that of the specimen used in this study and conventionally used JIS standard bolts will suffer from hydrogen embrittlement fracture if the bolts are used without corrosion inhibition and exposed to the environment directly.

3.4. Fracture surfaces observed by SEM

Figure 7 shows typical fracture surfaces of NIMS17 steel specimens with and without hydrogen. The specimen without hydrogen charging (figure 7(a)) shows dimple fracture, whereas the hydrogen-charged specimens (figures 7(b)–(d)) exhibit quasi-cleavage. No clear intergranular fracture surface, which is typical for hydrogen embrittlement fracture, was observed even for high hydrogen content. This implies an improved resistance of prior austenitic grain boundaries of NIMS17 steel to hydrogen embrittlement. Exposed specimens also show quasi-cleavage, as shown in figure 8 for a specimen exposed at Choshi for 3 months.

Figure 9. Relationships between fracture stress and hydrogen content of NIMS17 steel after hydrogen precharging, CCT and atmospheric exposure at Choshi and Tsukuba.

3.5. Relationships between fracture stress and hydrogen content for hydrogen-precharged and atmospherically corroded specimens

The relationships between fracture stress, $\sigma_f$, and hydrogen content, $H_E$, for specimens charged with hydrogen and corroded during CCT and atmospheric exposure are compared in figure 9. The fracture stresses of specimens corroded during CCT and atmospheric exposure tend to be lower than those of hydrogen-precharged specimens. This can probably be interpreted in terms of the less homogeneous hydrogen distribution of corroded specimens than that of hydrogen-precharged specimens. The hydrogen concentration near the surface including notch root, where crack initiates by hydrogen embrittlement, seems to be higher than those in other inner parts of the specimen and higher than the average hydrogen concentration measured by TDS. In contrast, when hydrogen charging was continued for 72 h by the cathodic hydrogen precharging procedure, the hydrogen distribution became more homogeneous than those of the atmospherically corroded specimens. The dissimilarity between hydrogen concentration at the crack initiation site and the apparent hydrogen concentration measured by TDS is responsible for the difference between hydrogen-precharged and corroded specimens. Different $\sigma_f$–$H_E$ relationships for the specimens corroded during CCT and outdoor exposure presumably originate from the dissimilar change in the notch root shape [15]. The corrosion rate is higher under CCT than under outdoor exposure. Therefore, the increase in notch root radius and concomitant decrease in stress concentration factor, $K_t$, are larger under CCT than under outdoor exposure. The larger decrease in $K_t$ seems to be responsible for the higher $\sigma_f$ for CCT than for outdoor exposure.

Although the quantitative measurement of hydrogen content by TDS is difficult under atmospheric corrosion condition [12, 15], the decrease in $\sigma_f$ can reflect the effect of hydrogen uptake caused by atmospheric corrosion. This gives us a more informative evaluation of hydrogen embrittlement
than either the $H_C$ measurement or comparison of $H_C$ and $H_E$ [6–8, 12–14]. In this manner, the method proposed in this study, namely, CCT or atmospheric exposure-SSRT in conjunction with TDS, is useful for evaluating hydrogen embrittlement.

4. Conclusions

The susceptibility of a prototype ultrahigh-strength (1700 MPa) steel NIMS17 to hydrogen embrittlement was studied using a slow strain rate test after hydrogen precharging, cyclic corrosion test and atmospheric exposure in conjunction with hydrogen measurement by thermal desorption spectroscopy. NIMS17 steel was successfully evaluated for hydrogen uptake caused by atmospheric corrosion and its effect on the mechanical properties. NIMS17 steel has a high critical diffusible hydrogen content for delayed fracture, $H_C$. The major reason for this is most probably the effect of hydrogen traps in the steel. Despite the high $H_C$, NIMS17 steel suffers from hydrogen embrittlement in an atmospheric corrosion environment, because the hydrogen traps enhance hydrogen absorption from the environment. As shown in the evaluation results, no beneficial effect of hydrogen traps in the steel is evident. The decrease in fracture stress during CCT was similar in the NIMS17 steel and AISI 4135 steel with a tensile strength of 1500 MPa, despite the fact that the susceptibility of a high-strength steel increases with its strength level. Therefore, the resistance of NIMS17 steel to hydrogen embrittlement is improved to a certain extent despite its ultrahigh strength.

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