Note

Application of NH_4SCN Aqueous Solution to Hydrogen Embrittlement Resistance Evaluation of Ultra-high Strength Steels

Shusaku TAKAGI¹⁾ and Yuki TOJI²⁾

1) Steel research laboratory, JFE Steel Corporation, 1, Kawasaki-cho, Chuo-ku, Chiba, 260-0835 Japan. E-mail: s-takagi@jfe-steel.co.jp

2) Steel research laboratory, JFE Steel Corporation, 1, Kokan-cho, Fukuyama, Hiroshima, 721-8510 Japan.

(Received on June 30, 2011; accepted on August 17, 2011)

KEY WORDS: delayed fracture; immersion-type hydrogen charging method; ammonium thiocyanate.

1. Background

It is well known that the risk of hydrogen embrittlement fracture becomes significant when ultra-high strength steels (UHSS) with tensile strength over 980 MPa are used in atmospheric corrosion environments.^{1,2)} Recently, application of UHSS sheets to automobiles has increased as a means of reducing auto body weight.³⁾ Although the hydrogen embrittlement resistance of UHSS sheets has been evaluated by various methods,^{4–12)} it is difficult to predict the risk of hydrogen embrittlement fracture quantitatively. In order to expand the automotive applications of UHSS sheets, precise prediction of the risk of hydrogen embrittlement fracture is important.

For evaluation of hydrogen embrittlement resistance, hydrogen must be charged to specimens. The immersion-type hydrogen charging method is more convenient than cathodic charging because a large number of specimens and automotive parts with various complex dimensions can be easily and uniformly charged with hydrogen at the same time simply by immersing the specimens in a solution. In contrast, the cathodic charging method requires various equipments, such as a power supply and electrodes, and the current density distribution in a specimen varies depending on the specimen shape. The latter point is important because the hydrogen charging condition in a specimen is considered to change depending on the local current density.

On the other hand, the immersion test also has a demerit, in that specimens dissolve during immersion because strong acids with pH in the range of 1 to 3 are generally used. Dissolution of the specimen surface causes changes in surface stress and microstructure conditions during the test. For example, surface stress is reduced and microcracks disappear. Therefore, if the immersion test is applied to hydrogen embrittlement resistance evaluation, it is very important to inhibit dissolution during testing and to understand the effect of any dissolution on hydrogen embrittlement resistance.

Recently, an ammonium thiocyanate (NH_4SCN) solution with a concentration of several percent has been used in hydrogen charging tests.¹³⁾ NH_4SCN is well known as a cat-

alyst in electrical hydrogen charging methods, and hydrogen embrittlement of bar steels is evaluated by the Fédération Internationale de la Précontrainte (FIP) test method, in which specimens are immersed in a 20% NH_4SCN solution at 323 K.¹⁴⁾ The pH of the 20% NH_4SCN solution is reported around 4–5, and low specimen dissolution is predicted due to higher pH than conventional hydrogen charging solutions as HCl with pH 1. This suggests the possibility of using a NH_4SCN solution in immersion tests for evaluation of hydrogen embrittlement in UHSS sheets with substantially reduced specimen dissolution. In this study, a low-dissolution hydrogen charging method was proposed.

2. Experimental Procedure

As test materials, 1180 MPa grade ferrite-martensite dual-phase steel (1180DP) was used. The chemical composition of the material was 0.13%C–1.4%Si–2.2%Mn steel. The hydrogen embrittlement resistances of the materials were evaluated by the U-bending method with the bending radius changed in the range from 2 to 10 mm. The U-bending specimen size was the width of 30 mm, the length of 100 mm and the thickness of 1.6 mm. Applied stress was measured by the X-ray method, and was 900 MPa.

The concentration of NH_4SCN was varied over a range from 0.01 to 20%. For comparison with the NH_4SCN solutions, conventional pH 1 and pH 3 HCl solutions were used. The solution volume was 500 ml per specimen and the solution volume to specimen area ratio was 7.8 ml/cm². For investigation of the effects of NH_4SCN concentration and pH of HCl on diffusible hydrogen entry in these steels, bent specimens without tightening by bolts were used. Normal tightened specimens were used in the evaluation of hydrogen embrittlement resistance. The testing temperature was 298 K, and the longest immersion time was 192 hours. The diffusible hydrogen content was measured by Thermal Desorption Analysis with a gas chromatograph. The heating rate was 200 K/hr. The diffusible hydrogen content was defined as the sum of the evolved hydrogen content up to 573 K, which corresponded to the end of the first peak of the hydrogen evolution curves. Specimens for hydrogen measurement were cut from the top of the U-bending specimens.

3. Experimental Results

3.1. Hydrogen Charging Method with NH_4SCN Solutions

3.1.1. Effect of NH_4SCN Concentration on Diffusible Hydrogen Entry in Steels

The effect of the NH_4SCN concentration of the solution on the diffusible hydrogen content and hydrogen embrittlement resistance was investigated. **Figure 1** shows the relationship between the NH_4SCN concentration and the diffusible hydrogen content entering the 1180DP specimens with a bending radius of 10 mm. As the NH_4SCN concentration increased, the diffusible hydrogen content also increased. With the 20% NH_4SCN solution, a diffusible hydrogen content of about 1.7 ppm could be charged in the specimen. The content of diffusible hydrogen charged in specimens can be controlled over a wide range by adjusting the NH_4SCN concentration. Regarding immersion time, the diffusible hydro-

Fig. 1. Influence of NH₄SCN concentration on diffusible hydrogen content of 1180DP with bending radius of 10 mm.

Fig. 2. Relationship between NH₄SCN concentration and pH.

gen content became saturated at 96 hours after the start of immersion.

In order to compare the diffusible hydrogen contents charged with a NH₄SCN solution and conventional solutions, the hydrogen charging results with immersion in pH 1 and pH 3 HCl solutions are plotted in Fig. 1. In the case of 1180DP, virtually the same diffusible hydrogen content could be charged with the 0.1% and 0.01% NH₄SCN solutions and the pH 1 and pH 3 HCl solutions, respectively. However, due to the different dissolution behaviors of materials, this relationship will depend on the chemical composition of the material being tested.

Figure 2 shows the relationship between the pH of the NH₄SCN solutions and the NH₄SCN concentration. The 20% NH₄SCN solution showed the lowest pH of 4.5 in this experiment. The hydrogen evolution curves of specimens charged with hydrogen by various methods are shown in **Fig. 3**. In addition to the results for specimens charged by immersion, the evolution curve of a specimen charged by the cathodic method was also plotted in this figure. Cathodic hydrogen charging was performed with an aqueous solution of 3% NaCl + 0.3% NH₄SCN at a current density of 0.1 A/m² for 48 hours. As the shapes and peak temperatures of the hydrogen evolution curves were virtually identical, it is considered that hydrogen was trapped at the same kind of trap site, independent of the hydrogen charging method.

Figure 4 shows the weight reduction of the specimens during the immersion tests. With the NH₄SCN solutions, weight reduction was extremely low in comparison with the

Fig. 3. Effect of hydrogen charging methods on hydrogen evolution curves. Hydrogen charging conditions. Immersion in 0.1% NH₄SCN : 48 h, Immersion in pH 1 HCl : 24 h Cathodic charging in 3% NaCl + 0.3% NH₄SCN at current density of 0.1 A/m² : 48 h.

Fig. 4. Dissolution of specimens in various solutions.

HCl solutions. For example, the weight reduction in the immersion test using the pH 1 HCl solution was 17% at 72 hours, whereas the weight reduction with the 0.1% NH₄SCN solution was only 0.08% at 96 hours. In terms of one-side surface dissolution rate, the specimen was dissolved about 2 $\mu\text{m/hr}$ in pH 1 HCl and about 0.007 $\mu\text{m/hr}$ in 0.1% NH₄SCN solution. This difference is due to the high pH of the 0.1% NH₄SCN solution (about pH 5.7) in comparison with the pH 1 HCl. **Figure 5** shows SEM micrographs of the surfaces of the untightened 1180DP specimens with the bending radius of 2 mm before and after immersion in the 0.1% NH₄SCN solution and pH 1 HCl solution. After immersion in the 0.1% NH₄SCN solution, the surface of the specimens had dissolved only slightly, but after immersion in the pH 1 HCl solution, the surface displayed remarkable dissolution during the immersion. Moreover, microcracks caused by bending were observed on the surface before immersion, and remained after immersion in 0.1% NH₄SCN. However, after immersion in pH 1 HCl, the microcracks had been eliminated by dissolution of the surface.

Table 1 shows the evaluation results of hydrogen embrit-

Fig. 5. Surface change of specimens before and after immersion tests.

Table 1. Evaluation of hydrogen embrittlement fracture condition of 1180DP by immersion in pH 1 HCl solution and 0.1% NH_4SCN solution. (N: No failure, F: Failure)

Bending radius/mm	2	3	4	5	7	10
pH-1 HCl	F	F	N	N	N	N
0.1% NH_4SCN	F	N	N	N	N	N

tlement resistance of 1180DP with the 0.1% NH_4SCN solutions and pH 1 HCl solutions. In spite of the large difference in dissolution of the specimens, the hydrogen embrittlement failure limits were almost the same with these solutions under the condition that the same diffusible hydrogen content was charged. It is conjectured the microcrack initiation rate and crack propagation rate were higher than the surface dissolution rate. The influence of dissolution of specimens on hydrogen embrittlement evaluation results should be investigated to use the immersion-type hydrogen charging method more appropriately.

Based on the results described in this section, it is judged that the NH_4SCN solution can be used for evaluation of the hydrogen embrittlement resistance of UHSS sheets with low dissolution.

4. Conclusion

With the aim of establishing an easy and precise hydrogen embrittlement evaluation method with immersion hydrogen charging, a hydrogen charging method with low dissolution of specimens was proposed. The following results were obtained.

(1) Using a NH_4SCN solution with a concentration of less than 20%, the diffusible hydrogen content entering specimens can be controlled over a wide range by adjusting the concentration of the NH_4SCN solution.

(2) Analysis of the shapes and peak temperatures of hydrogen evolution curves showed that diffusible hydrogen was trapped at the same kind of trap site, independent of the hydrogen charging method.

(3) The possibility of easy and precise hydrogen embrittlement evaluation using the NH_4SCN solution was demonstrated.

REFERENCES

- 1) S. Matsuyama: Delayed Fracture, The Nikkan Kogyo Shimbun, LTD., Tokyo, (1989), 25.
- 2) Detroit Free Press, **194** (1981), No. 296 (1981.2.24.Tues.).
- 3) Y. Toji, K. Hasegawa, H. Shigemoto, H. Kawabe, T. Fujita, Y. Tanaka, H. Nakamura, H. Ishida and H. Sakamoto: *Rev. Automot. Eng.*, **30** (2009), 159.
- 4) Y. Toji, S. Takagi, M. Yoshino, K. Hasegawa and Y. Tanaka: *Tetsu-to-Hagané*, **95** (2009), 887.
- 5) Y. Toji, S. Takagi, M. Yoshino, K. Hasegawa and Y. Tanaka: *Mater. Sci. Forum*, **638-642** (2010), 3537.
- 6) S. Takagi, Y. Toji, K. Hasegawa, Y. Tanaka, N. Rössler, B. Hammer and T. Heller: *Inter. J. Automot. Eng.*, **2** (2010), 7.
- 7) Y. Hosoya, S. Tsuyama, Y. Nagataki, S. Kanetoh, T. Izuishi and Y. Takada: *NKK Tech. Rep.*, **145** (1994), 33.
- 8) J. Iwaya, Y. Okano, H. Shirasawa and S. Sawaki: *Kobe Steel Eng. Rep.*, **47-2** (1997), 42.
- 9) K. Yamazaki and Y. Mizuyama: *Tetsu-to-Hagané*, **83** (1997), 754.
- 10) N. Kojima: *Press Gijyutu*, **42** (2004), 38.
- 11) K. Hayashi, N. Fujita, S. Takebayashi, M. Takahashi and Y. Sakuma: *Spec. Publ. Soc. Automot. Eng.*, **SP-1954** (2005), 25.
- 12) Y. Mukai: *Kobe Steel Eng. Rep.*, **55-2** (2005), 30.
- 13) H. Suzuki and K. Takai: *ISIJ Int.*, **52** (2012), 174.
- 14) Fédération Internationale de la Précontrainte: Report on Prestressing Steel: 5. Stress Corrosion Cracking Resistance Test for Prestressing Tendons, Vol. 5 (1980).