Effect of Applied Cathodic Potential on Susceptibility to Hydrogen Embrittlement in High Strength Low Alloy Steel

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In order to investigate the effects of applied cathodic potential and chemical hydrogen absorption promoter (thiourea) on the susceptibility to hydrogen embrittlement of the high strength low alloy (HSLA) steel, slow strain rate tensile (SSRT) tests were conducted in various buffer aqueous solutions of pH 10.0. During SSRT tests, the specimens were cathodically polarized under potentiostatic control. Polarization levels were varied from the corrosion potential ($E_{\text{corr}}$) to hydrogen gas evolution potential ($E_{\text{H2gas}}$), including the adsorbed hydrogen potential ($E_{\text{Hads}}$) determined by cyclic voltammetry (CV). Additionally, thermal desorption spectroscopic (TDS) analyses were applied to the specimens fractured by SSRT test and the dependence of hydrogen absorption characteristic on applied potential was also examined for understanding the SSRT test results. Experimental results revealed that the hydrogen embrittlement behavior was strongly dependent on the applied cathodic potential. In the $E_{\text{Hads}}$ region, the susceptibility to hydrogen embrittlement increased with increasing cathodic overpotential. On the other hand, in the $E_{\text{H2gas}}$ region, the susceptibility was independent of the applied potential. Moreover, by adding thiourea to the solution, the susceptibility to hydrogen embrittlement increased slightly in the $E_{\text{H2gas}}$ region compared with that in the solution without thiourea.

The potential dependence of hydrogen embrittlement was closely associated with the variation in hydrogen absorption rate under applied potential.

KEY WORDS: hydrogen embrittlement; high strength low alloy steel; slow strain rate tensile test; cyclic voltammetry; thermal desorption spectroscopic analysis; potential dependence; hydrogen gas evolution; adsorbed hydrogen; hydrogen absorption.

1. Introduction

It is well known that the susceptibility of high strength steels to hydrogen embrittlement (delayed fracture) increases with increasing strength level of steels, resulting in a great hindrance to practical application of high strength steels. The sequential steps in hydrogen embrittlement process consist of generation of adsorbed hydrogen due to wet corrosion in thin layer of water/aqueous solution, absorption of hydrogen into the steel, lattice diffusion of atomic hydrogen, segregation and accumulation of a sufficient concentration of hydrogen at a susceptible metallurgical site, and subsequent cracking. The increase in fractional hydrogen surface coverage (amount of adsorbed hydrogen) seems to lead to the increase in hydrogen concentration in the steel and then to cause a premature cracking.

In general, the hydrogen adsorption/absorption process progresses at the vicinity of corrosion potential ($E_{\text{corr}}$) in an actual natural environment. But, most of earlier experiments on hydrogen embrittlement had been carried out at the cathodic polarized potential where the evolution of hydrogen gas occurs. Hydrogen embrittlement behavior at the adsorbed hydrogen potential ($E_{\text{Hads}}$), which lies between the $E_{\text{corr}}$ and the hydrogen gas evolution potential ($E_{\text{H2gas}}$), has not been widely reported. It is expected to obtain an important information necessary for clarifying the entire process and mechanism of hydrogen embrittlement if the relationship between the hydrogen adsorption/absorption characteristics and the susceptibility to hydrogen embrittlement in the potential range from the $E_{\text{corr}}$ to the $E_{\text{Hads}}$ is revealed.

In this study, in order to investigate the effects of applied cathodic potential and chemical hydrogen absorption promoter (thiourea) on the susceptibility to hydrogen embrittlement of the high strength low alloy (HSLA) steel, slow strain rate tensile (SSRT) tests were conducted in buffer aqueous solutions of pH 10.0 in the potential range from the $E_{\text{corr}}$ to the $E_{\text{H2gas}}$, including the $E_{\text{Hads}}$ determined by cyclic voltammetry (CV). Additionally, thermal desorption spectroscopic (TDS) analyses were applied to the specimens fractured by SSRT test and the dependence of hydrogen absorption characteristic on applied potential was also examined for understanding the SSRT test results.
2. Experimental Procedure

2.1. Material and Test Solutions

The material used in this study was a vanadium-added high strength low alloy (HSLA) steel. Chemical composition and heat treatment of the steel and its mechanical properties at room temperature are given in Tables 1 and 2, respectively.

As illustrated in Fig. 1, the CV and SSRT tests were carried out in buffer aqueous solutions of pH 10.0 at 298 K in which iron is immune to corrosion. Three kinds of buffer aqueous solutions were used in the present study, boric acid/borax (H₃BO₃/Na₂B₄O₇), sodium hydrogencarbonate/sodium carbonate (NaHCO₃/Na₂CO₃) and disodium hydrogenphosphate/trisodium phosphate (Na₂HPO₄/Na₃PO₄) buffer aqueous solutions. Furthermore, the tests were also performed in the boric acid/borax buffer aqueous solution containing thiourea (0.02 kmol/m³) to examine the effect of chemical hydrogen adsorption promoter on the susceptibility to hydrogen embrittlement. The concentration of each buffer aqueous solution is summarized in Table 3.

2.2. Cyclic Voltammetry (CV)

The plate-type CV samples, 10×10×0.5 mm, were connected to a lead wire and then covered with epoxy resin, except for the measurement area of 9×9 mm. The CVs were performed at a sweep rate of 10 mV/s in the buffer aqueous solutions at 298 K. Before performing the measurements the solution was de-aerated with nitrogen gas, and the gas was constantly passed through during the measurements.

2.3. Slow Strain Rate Tensile (SSRT) Test

A smooth-cylindrical-type specimen was covered with epoxy resin and paraffin, except for the gauge portion (φ2 mm, G. L. 15 mm) and was subjected to the SSRT test. The SSRT tests were performed at a strain rate of 10⁻⁶ s⁻¹ and a temperature of 298±1 K. During straining, the test specimens were cathodically polarized under potentiostatic control. The applied potential used in this study was changed over the range from −0.26 to −1.16 V (vs. NHE). Electrolytes were de-aerated with nitrogen gas both before and during the SSRT test. The time to failure, tₑ, and the maximum stress, σ_max, were used as parameters of the susceptibility to hydrogen embrittlement.

2.4. Thermal Desorption Spectroscopic (TDS) Analysis

The TDS analyses were carried out from room temperature to 1 073 K to investigate hydrogen release behavior from trapping sites in the steel. The heating rate used in this study was 200 K/h. The desorbed hydrogen carried with high purity argon gas was detected by a gas chromatograph every 5 min. The flow rate of the argon carrier gas was fixed at 1.2×10⁻³ m³/min throughout the analysis. The hydrogen evolution rate was defined as the amount of hydrogen desorbed in one minute per one gram of the specimen.

3. Results and Discussion

3.1. Effects of Anion and Thiourea on CV Characteristics

Figure 2 shows typical examples of cyclic voltammograms (CV) measured in the three kinds of buffer aqueous solutions. These CVs were measured in the potential range from −0.70 to −0.85 V (vs. NHE). The overall cathodic current densities decrease in all solutions as the number of cycle increases. These decreases are likely to result from the reduction reaction of oxide films, which had been formed in atmosphere. However, the decrease in cathodic current density in the sodium hydrogencarbonate/sodium carbonate (NaHCO₃/Na₂CO₃) is slower than those in the other solutions. This sluggish decrease is considered to be attributable to relatively thick and slightly soluble oxide films composed of FeO₃ or FeCO₃, which had been formed in the solution before the measurements, in view of fact that the potential range from E_corr to −0.7 V lies in the domain of FeO₃ or FeCO₃ in the E–pH equilibrium diagram for Fe–H₂O system. Actually FeO₃ and FeCO₃ were detected on the SSRT specimen surfaces tested at potential range from E_corr to −0.56 V in the sodium hydrogen carbonate/sodium carbonate by Raman spectroscopy. It is presumed that the cathodic current density in the sodium
hydrogencarbonate/sodium carbonate reaches the levels of those in the other solutions if the number of cyclic increases further. Therefore, it is desirable to use the boric acid/borax or the disodium hydrogenphosphate/trisodium phosphate buffer aqueous solutions to investigate the hydrogen adsorption characteristics.

**Figure 3** shows CVs measured in the potential range from the $E_{\text{corr}}$ to the $E_{\text{H}_2\text{gas}}$ in the boric acid/borax buffer aqueous solutions with and without thiourea. These CVs were measured after repeating the CV in the potential range from $-0.70$ to $-0.85$ V for reducing oxide films. It is obvious from this figure that the potential at which a cathodic current rises suddenly is shifted about $-0.2$ V lower by adding thiourea to the solution. This result means that the addition of thiourea increases the overpotential for hydrogen gas evolution resulting in the depression of hydrogen gas evolution.\(^{10}\) Thus, there is a strong likelihood that the addition of thiourea increases hydrogen surface coverage (amount of adsorbed hydrogen).\(^{11}\) This increase also leads to increase hydrogen concentration at subsurface, which is just equilibrated with the hydrogen surface coverage.

In this paper, two different potential regions are expediently defined as adsorbed hydrogen potential ($E_{\text{H}_{\text{ads}}}$) and hydrogen gas evolution one ($E_{\text{H}_2\text{gas}}$), respectively, on the basis of the potential at which the rapid increase of cathodic current appears. On the other hand, the latter one is more negative than the potential where the evolution of hydrogen gas can be distinctively observed in this potential.

### 3.2. Effect of Applied Potential on Susceptibility to Hydrogen Embrittlement

Based on the results obtained from the CV measurements, a slow strain rate tensile (SSRT) test was carried out under potentiostatic control over the range from $-0.26$ to $-1.16$ V (vs. NHE). **Figure 4** shows typical examples of load-displacement curves along with a curve in air. The curves were measured at $-0.36$ and $-0.91$ V vs. NHE in the boric acid/borax buffer aqueous solutions (pH 10.0) at 298 K.
as that tested in air. On the other hand, the load suddenly drops at a certain load level without enough ductility under potentiostatic control at −0.91 V where the hydrogen gas evolution can be clearly observed.

**Figure 5** shows fracture surfaces of the specimens tested at −0.36, −0.76 and −1.16 V in the boric acid/borax buffer aqueous solution. The fracture mode of the specimen tested at −0.36 V is typical ductile transgranular, while the fractures occur in a brittle manner in the specimens tested at −0.76 and −1.16 V. These brittle fracture surfaces exhibit quasi-cleavage and intergranular modes characterizing hydrogen embrittlement of high strength steels.

The SSRT test results obtained in the three kinds of buffer aqueous solutions of pH 10.0 are given in **Fig. 6**, along with the results obtained from the tests under galvanostatic control at 5 and −10 A/m². The time to failure, \( t_f \), and the maximum stress, \( \sigma_{\text{max}} \), are plotted as a function of applied potential. **Figure 7** shows the electric charge required for failure. It is apparent from Fig. 6 that \( \sigma_{\text{max}} \) hardly depends on not only kind of buffer aqueous solution but also applied potential. In contrast to the \( \sigma_{\text{max}} \), the \( t_f \) shows the distinct potential dependence and decreases monotonously with increasing cathodic overpotential in the \( E_{\text{Hads}} \) region, i.e., −0.26 to −0.8 V. However, in more negative potential region, namely, at the \( E_{\text{H,\text{gas}}} \) (−0.8 V), it seems unaffected by the applied potential and tends to maintain a relatively low value. The difference of buffer aqueous solution has almost no influence on the change in \( t_f \) as well as \( \sigma_{\text{max}} \). The potential of −0.8 V, which distinguishes the above two types of hydrogen embrittlement, can be also clearly seen as a break in Fig. 7. As mentioned in Sec. 3.1, the CV characteristics in the sodium hydrogencarbonate/sodium carbonate (NaHCO\(_3\)/Na\(_2\)CO\(_3\)) were different from those in the other two kinds of solutions. But, the influences of anion on the susceptibility to hydrogen embrittlement were not observed in this study.

The potentials measured during the SSRT tests under galvanostatic control at 5 and −10 A/m² showed around −0.91 and −0.99 V, respectively. It is found that conventional accelerated hydrogen embrittlement tests under galvanostatic control where the evolution of hydrogen gas can be clearly seen correspond to the tests in the \( E_{\text{H,\text{gas}}} \) region.
3.3. Effect of Thiourea on Susceptibility to Hydrogen Embrittlement

Figure 8 shows the influence of chemical hydrogen absorption promoter, thiourea, on the susceptibility to hydrogen embrittlement in the boric acid/borax buffer aqueous solution. The maximum stress, $\sigma_{\text{max}}$, measured in the boric acid/borax buffer aqueous solution shows almost no variation, whereas that in the thiourea-added solution has a tendency to decrease gradually with decreasing applied potential. On the other hand, the times to failure, $t_f$, in the solutions with and without thiourea decrease with increasing cathodic overpotential in each $E_{\text{Hads}}$ region, and almost constant in their $E_{\text{H$_2$gas}}$ regions. However, the $t_f$ is found to be slightly shorter in the $E_{\text{H$_2$gas}}$ region by adding the thiourea to the solution although the $t_f$ in the $E_{\text{Hads}}$ region is hardly affected. This shorter $t_f$ accompanied with the lower maximum tensile stress seems to be closely associated with the increase in hydrogen adsorption as mentioned before.

Moreover, it seems that the addition of thiourea shifts the potential which distinguishes the two different types of hydrogen embrittlement, corresponding to the CV characteristics. This shift can be observed in the variation of electric charge necessary for failure with applied potential in Fig. 9.

3.4. Relationship between Hydrogen Absorption Characteristic and Susceptibility to Hydrogen Embrittlement

In general, the susceptibility to hydrogen embrittlement increases as the hydrogen content in steel increases. Some researchers have tried to evaluate the hydrogen embrittlement susceptibility of high strength steels from the viewpoint of the critical diffusible hydrogen concentration. In order to understand the present hydrogen embrittlement behavior of the HSLA steel, the dependence of hydrogen absorption on applied potential was investigated by the thermal desorption spectroscopic (TDS) analyses.

Figure 10 shows examples of hydrogen evolution curves measured after the SSRT tests. The peaks of hydrogen evolution rate, which are attributable to diffusible hydrogen, appear at around 373–393 K in the specimens tested at $E_{\text{H$_2$gas}}$ in the boric acid/borax buffer aqueous solution and in the thiourea-added one. The peak values measured on the specimens tested at $-1.16$ V are clearly higher than those at $-0.76$ V.

The diffusible hydrogen content in the steel, $C_H$, was calculated from the area under hydrogen evolution curve up to 573 K. The obtained $C_H$ is plotted as a function of applied potential in Fig. 11. The $C_H$ has a tendency to increase monotonously with increasing cathodic overpotential in more negative potential region than $-0.56$ V. It can be also found
that the $C_H$ measured on the specimens tested in the thiourea-added solution is slightly lower than that in the solution without thiourea. The amount of hydrogen absorption per unit time was determined by normalizing the diffusible hydrogen content $C_H$ by the time to failure $t_f$ and was termed the hydrogen absorption rate, $C_H/t_f$. 

Figure 12 shows the $C_H/t_f$ plotted as a function of applied potential. As mentioned in Sec. 3.1, it was considered that the addition of thiourea increased hydrogen concentration in the steel because it suppressed the hydrogen gas evolution resulting in the increase in hydrogen surface coverage (amount of adsorbed hydrogen). Actually, as can be seen in Fig. 12, the $C_H/t_f$ in the solution with thiourea is slightly larger than that in the solution without thiourea at the $E_{H_{2}gas}$ ($-1.16$ V) although there is no such an increase in $C_H/t_f$ due to the addition of thiourea at the $E_{Hads}$.

Figure 13 shows the relationship between the obtained $C_H/t_f$ and the time to failure $t_f$. It can be clearly seen that the $t_f$ decreases monotonically as the $C_H/t_f$ increases. This result suggests that the potential dependence of hydrogen embrittlement results from the variation in amount of hydrogen absorption per unit time under applied potential. That is, larger cathodic overpotential accelerates the absorption of hydrogen into the steel, with the result that the susceptibility to hydrogen embrittlement increases. However, the decrease in $t_f$ seems to be slightly dependent with the addition of thiourea although the number of data is not sufficient to conclude. The $t_f$ has a tendency to be shorter in the thiourea-added solution than in the solution without thiourea. This deviation may indicate that the potential dependence of hydrogen embrittlement cannot explain by only the change in amount of hydrogen absorption per unit time and the other factors also have an effect on that.

It is obvious from Fig. 1 that the $E_{H_{2}gas}$ region lies in the immunity domain of iron, while the steel exhibits passivity.
in the major part of the $E_{\text{Hads}}$ region. Nakasa et al.\textsuperscript{17,18}\ reported that the delayed fracture was accelerated by the superposition of small cyclic stress on the constant stress. This acceleration resulted from the promotion of corrosion reaction and hydrogen absorption which was attributed to localized breakdown of passive film. Conversely, the absorption of hydrogen in steel can be retarded by the formation of passive film if it has protection nature. That is, there is a possibility that the change in state of passive film with applied cathodic potential, such as a composition, microstructure and thickness, influences hydrogen absorption/adsorption process and then causes the present potential dependence of hydrogen embrittlement. It seems to be also necessary to examine the effect of passive film on absorption of atomic hydrogen on the specimen surface and/or absorption of hydrogen into the steel for much better understanding of the potential dependence of the susceptibility to hydrogen embrittlement. Further study based on the variation in apparent diffusion rate of hydrogen through passive film with applied potential is in progress.

4. Conclusions

The hydrogen embrittlement behavior in the high strength low alloy (HSLA) steel is strongly dependent on the applied cathodic potential. Especially in the adsorbed hydrogen potential ($E_{\text{Hads}}$) region, the susceptibility to hydrogen embrittlement increases with increasing cathodic overpotential. On the other hand, in the hydrogen gas evolution potential ($E_{\text{H}_2\text{gas}}$) region, the susceptibility is independent of applied potential. Furthermore, by adding thiourea to the solution, the susceptibility increases slightly in the $E_{\text{H}_2\text{gas}}$ region compared with that in the solution without thiourea. There is a relatively good correlation between the amount of hydrogen absorption per unit time ($C_{\text{H}}/t_1$) and the time to failure ($t_f$), and the susceptibility to hydrogen embrittlement has a tendency to increase monotonically with increasing $C_{\text{H}}/t_1$. As a consequence, the potential dependence of hydrogen embrittlement is closely associated with the variation in hydrogen absorption rate under applied potential.

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REFERENCES

1) S. Matsuyama: Delayed Fracture, The Nikkan Kogyo Shimbun, Ltd., Tokyo, (1989), 25.
2) J. R. Scully and P. J. Moran: Corrosion, 44 (1988), 176.
3) Advanced in Delayed Fracture Solution, ISIJ, Tokyo, (1997), 1.
4) W.-T. Tsai and S.-L. Chou: Corros. Sci., 42 (2000), 1741.
5) M. Pourbaix: Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, Oxford, (1966), 307.
6) T. Misawa: Corros. Sci., 13 (1973), 659.
7) N. Suzuki, T. Miyagawa, S. Gotoh and T. Takahashi: Wire J. Int., 11 (1986), 36.
8) M. Nagumo, M. Nakamura and K. Takai: Metall. Mater. Trans. A, 32 (2001), 339.
9) T. Kodama: Proc. of 47th JSCE Corros. Eng. Symp., JSCE, Tokyo, (1983), 1.
10) M. Kondo, N. Yuki, K. Sasaki and T. Otsuka: Proc. of the 47th Japan Conf. on Materials and Environments, JSCE, Tokyo, (2000), 95.
11) Synthetic Materials Strength 7—Environmental and High Temperature Strength, Ohm, Ltd., Tokyo, (1984), 54.
12) T. Kushida and T. Kudo: Materia Jpn., 33 (1994), 932.
13) S. Yamasaki and T. Takahashi: Tetsu-to-Hagané, 83 (1997), 454.
14) S. Takagi, T. Inoue, T. Hara, M. Hayakawa, K. Tsuzaki and T. Takahashi: Tetsu-to-Hagané, 86 (2000), 689.
15) T. Shiraga and T. Yokota: Report on Function of Hydrogen in Environmental Embrittlement of Structural Materials II, ISIJ, Tokyo, (2000), 51.
16) S. Komazaki, A. Koyama and T. Misawa: Mater. Trans. JIM, 43 (2002), 2213.
17) K. Nakasa, M. Kidoh and H. Takei: Jpn. J. Inst. Met., 40 (1976), 744.
18) M. Kidoh, K. Nakasa and H. Takei: Tetsu-to-Hagané, 65 (1979), 535.