Effects of Test Conditions on Corrosion Reactions and Hydrogen Absorption in Hydrogen Embrittlement Tests Using an Ammonium Thiocyanate Solution

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Ammonium thiocyanate is widely used as a reagent for promoting hydrogen absorption by high-strength steels. The effects of the solution concentration, temperature and dissolved oxygen on corrosion film formation, corrosion reactions and hydrogen absorption were investigated in a hydrogen embrittlement test environment using an ammonium thiocyanate aqueous solution. A still bath of a 20 mass% ammonium thiocyanate solution displayed a supply limitation, whereas a solution with flow influenced the corrosion and hydrogen absorption by the tested steel. The concentration of dissolved oxygen that forms an iron oxide film was found to have a small effect on hydrogen absorption. The change in the hydrogen content of the tested steel with elapsed time is explained in terms of changes in the equilibrium concentration of hydrogen on the steel surface and in the corrosion rate. The change in the solution pH during potentiostatic electrolysis tests in an ammonium thiocyanate solution is also discussed.

KEY WORDS: corrosion; hydrogen embrittlement; martensitic steels; hydrogen; electrochemistry; ammonium thiocyanate; TDA; hydrogen diffusion; hydrogen charging.

1. Introduction

Ammonium thiocyanate (NH₄SCN) is widely used as a reagent for charging steel materials with hydrogen because of its effect on promoting hydrogen absorption and its ease of use. A well-known hydrogen embrittlement test using NH₄SCN is conducted under constant loading in a 20 mass% NH₄SCN aqueous solution at 50°C to evaluate the time to rupture.¹⁻³ This test method is referred to as the FIP test because it was standardized by the Fédération Internationale de la Précontrainte (FIP).¹ Numerous tests have been conducted to investigate the influence of the tested materials and the test conditions on the time to rupture in this test procedure.¹⁻¹¹ The authors previously reported that hydrogen absorption during an immersion test in an NH₄SCN aqueous solution is affected by corrosion reactions and the resultant corrosion products.⁴⁻⁵ Reported examples of corrosion reactions of steel materials in an NH₄SCN aqueous solution include the dissolution of iron as an anodic reaction and a reduction reaction of dissolved oxygen and a simple reduction reaction of protons as cathodic reactions.¹ The authors reported that two types of reactions mainly take place in parallel as cathodic reactions of steel materials in an NH₄SCN aqueous solution.⁶ One is a reduction reaction of dissolved oxygen and the other is a cathodic reaction accompanying the decomposition of thiocyanate ion (SCN⁻). It has been reported that this cathodic reaction accompanying the decomposition of SCN⁻ promotes hydrogen absorption⁷ and simultaneously lowers the reaction rate and forms a corrosion film containing Fe, S and O due to the rise in the solution pH because the reaction consumes hydrogen.⁷ Reported corrosion reaction products include Fe₃S₄ and Fe₃[Fe(CN)₆]₃¹⁻¹⁵ as well as FeS and S⁰.⁵ Iron sulfides, including FeS, iron sulfates and iron oxides were detected in a corrosion film that formed on the steel surface in the initial phase of the corrosion reaction, suggesting the possibility that various types of elementary reactions take place as cathodic reactions accompanying the decomposition of SCN⁻.⁷

There are many reports about electrolytic hydrogen charging in electrochemical tests using a single steel electrode in a NH₄SCN solution.⁸ However, most of the reports concern the electrolysis conditions and the amount of hydrogen charged to the tested materials. There are only a few reports that also deal with the decomposition reaction of SCN⁻ at the cathode and changes in the solution accompanying corrosion reactions.

Hydrogen absorption in an NH₄SCN aqueous solution is affected by the corrosion film and the solution pH that is related to the formation of the film.⁴⁻⁵ In order to
understand the effect of the corrosion film on hydrogen absorption, it is important to elucidate the influence of the solution concentration, temperature and dissolved oxygen on corrosion reactions and corrosion film formation. There have been reports so far concerning the effect of the test conditions on the time to rupture in the FIP test\(^{1,3}\) but only a few reports have focused on corrosion reactions.

This paper reports the effects of the solution concentration, temperature and dissolved oxygen on the time to rupture, corrosion film formation, corrosion reactions and hydrogen absorption in the FIP test environment using a NH\(_4\)SCN aqueous solution.

2. Experimental Method

2.1. Tested Material

The tested material was tempered martensitic PC steel corresponding to Type D, Class 1 steel as specified in Japanese Industrial Standard JIS G 3137 (Small diameter steel bars for prestressed concrete). The steel was formed into round bars of 7.1 mm in diameter and no irregular shape was machined in the surface. The chemical composition of the tested steel is shown in Table 1 and its mechanical properties are given in Table 2. The principal element added to the tested steel was Si of approximately 1%, and its tensile strength was 1 455 MPa.

2.2. Hydrogen Embrittlement Tests

Hydrogen embrittlement tests were conducted according to JSCE S 1201 that prescribes the FIP test procedure.\(^{3}\) The basic test conditions were a 20 mass% NH\(_4\)SCN solution at 50°C, a solution volume-to-specimen surface area of 10 ml/cm\(^2\), and an applied load of 70% of the tensile strength. Tests were conducted under constant loading for 200 h to evaluate the time to rupture. The concentration of the NH\(_4\)SCN solution was varied among 2, 10, 15, 18 and 20 mass\% to evaluate its effect. The solution temperature was varied among 45, 50, 55 and 60°C for the same purpose.

2.3. Immersion Tests

The basic conditions of the immersion tests were a 20 mass\% NH\(_4\)SCN solution at 50°C, a solution volume-to-specimen surface area of 10 ml/cm\(^2\), a still bath, a hermetic condition and an immersion time of 24 h. The concentration of the NH\(_4\)SCN solution was varied among 2, 10, 15, 18 and 20 mass\% to evaluate its effect. The solution temperature was varied among 30, 50 and 70°C for periods ranging from 0 to 144 h and the quantity of desorbed hydrogen was analyzed by TDA.

Table 1. Chemical composition of the tested prestressing steel.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ti</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>0.31</td>
<td>1.03</td>
<td>0.73</td>
<td>0.017</td>
<td>0.007</td>
<td>0.01</td>
<td>0.02</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

Table 2. Mechanical properties of the tested prestressing steel.

<table>
<thead>
<tr>
<th>Diameter [mm]</th>
<th>Tensile Strength [MPa]</th>
<th>0.2% Proof Strength [MPa]</th>
<th>Elongation [%]</th>
<th>Reduction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>1 455</td>
<td>1 356</td>
<td>10.6</td>
<td>66</td>
</tr>
</tbody>
</table>

2.4. Measurement of Hydrogen Diffusion Coefficient of Steel Specimens

The apparent hydrogen diffusion coefficient was measured from the decrease in the hydrogen content of steel specimens that were initially charged with a certain quantity of hydrogen and then kept at a specified temperature. The specimens were charged with 2.4 mass ppm of hydrogen under conditions of a 20 mass\% NH\(_4\)SCN aqueous solution at 50°C for 96 h of immersion. Following hydrogen charging, the specimens were kept in a constant temperature chamber at temperatures of 30, 50 and 70°C for periods ranging from 0 to 144 h and the quantity of desorbed hydrogen was analyzed by TDA.

2.5. Polarization Measurements

Polarization measurements were made for cross sections of the steel specimens. A glass single chamber type electrochemical cell, all electrodes mounted in, was used. After the electrodes were polished with wet emery paper, washed with water and dried, the spontaneous potential was first measured in the test solution for 600 s, and then polarization measurements were performed from the spontaneous potential. The basic polarization measurement conditions were a 20 mass\% NH\(_4\)SCN solution at 50°C, a solution volume-to-specimen surface area of approximately 2 500 ml/cm\(^2\), a still bath, and Ar deaeration. Some measurements were also made under a condition where the gas phase portion was open to the air, a condition where flow was applied by stirring the solution in the cell with a magnetic stirrer, under different temperature conditions of 30°C and 70°C, and under different NH\(_4\)SCN solution concentrations of 0.5 mass\% and 2 mass\%. A saturated calomel electrode (SCE) was used as the reference electrode and the potential scan rate was 20 mV/min. In the tests conducted to investigate the effects of the solution concentration and stirring, the solution was sampled near the counter electrode following the test and the solution pH was measured at room temperature to determine the change in the pH compared with that before the polarization measurement.
2.6. Potentiostatic Electrolysis Tests

Potentiostatic electrolysis tests were conducted to evaluate the reactions occurring on the respective electrodes. A glass separate chamber type electrochemical cell was used in which the working electrode chamber and the counter electrode chamber were connected by porous glass. The solution conditions for electrolysis were a 20 mass% NH₄SCN aqueous solution at 50°C, 80 ml of solution in the working electrode chamber and in the counter electrode chamber, an air atmosphere and a still bath. The working and counter electrodes were made of either steel or platinum. The surface area of the Pt electrode was 4 cm² and that of the steel electrode was 2 cm². The condition for potentiostatic electrolysis was a potential of −1.542 V vs. SCE at the steel working electrode. Measurements were made of the current during 2 h of electrolysis and of the solution pH in the working electrode and counter electrode chambers.

Following the test, the hydrogen gas in the gas phase portion of the cell and SO₄²⁻ ions in the solution were analyzed. The hydrogen gas analysis was not quantitative because the tests were conducted under a semi-hermetic condition.

3. Results and Discussion

3.1. Effect of NH₄SCN Concentration on Steel Surface

Figure 1 shows the effect of the NH₄SCN solution concentration on the time to rupture in the hydrogen embrittlement tests conducted under the conditions described in subsection 2.2. A time to rupture of approximately 120 h is seen for the FIP test condition of a 20 mass% NH₄SCN solution. The time to rupture did not change with the 15 mass% NH₄SCN solution, but with a solution concentration of 10 mass% it increased by 30 h and with the 2 mass% solution it exceeded the test termination time of 200 h. The consumption of NH₄SCN accompanying corrosion of the steel specimens in the 20 mass% NH₄SCN solution at 50°C was estimated to be less than 2 mass% even after an elapsed time of 200 h. This indicates that consumption of NH₄SCN during hydrogen embrittlement testing has a negligible effect on the time to rupture.

Figure 2 shows the effect of the NH₄SCN solution concentration on the hydrogen content and weight loss of the steel specimens due to corrosion during the immersion tests. The immersion time was set at 24 h, which is the length of time at which the same type of tempered martensitic steel as that used in this study reached its maximum hydrogen content. Under the deaeration condition, the hydrogen content (Fig. 2(1)) and weight loss (Fig. 2(2)) of the steel specimens increased with a higher NH₄SCN solution concentration. Immersion tests were also conducted in an air atmosphere using NH₄SCN solution concentrations of 0.5 and 2 mass%. The weight loss due to corrosion in the air atmosphere increased by 30% to 120% compared with the results obtained in the deaeration atmosphere, but the hydrogen content of the steel increased only slightly by less than 8%. Because all of the test specimens displayed a black color following the immersion tests, it was inferred that iron sulfides and iron oxides formed on the surface. The authors previously reported that the corrosion rate in a deaeration atmosphere, although the increase in the hydrogen content of the tested steel remained at about 5%. These results indicated that, with a low NH₄SCN solution concentration where a small quantity of hydrogen is absorbed, dissolved oxygen has a large effect on the corrosion rate of the steel, but the reduction reaction of dissolved oxygen has a small effect on hydrogen absorption.

The authors previously reported that the principal corrosion reactions of PC steel in a NH₄SCN solution are the anodic reaction in Eq. (1), the reduction reaction of dissolved oxygen shown in Eq. (2) and the reaction in Eq. (3) that accompanies the decomposition of SCN⁻, the latter two being cathodic reactions:

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- & \text{............... (1)} \\
\text{H}_2\text{O} + 1/2\text{O}_2 + 2e^- & \rightarrow 2\text{OH}^- & \text{............... (2)} \\
\text{SCN}^- + 2\text{H}_2\text{O} + 2\text{H}^+ + 2e^- & \rightarrow \text{S}^{2-} + \text{H}_2 + \text{CO}_2 + \text{NH}_4^+ & \text{............... (3)}
\end{align*}
\]

Sulfur oxides were also detected in an analysis of the corrosion film, suggesting the possibility that various types
of corrosion reactions take place in the NH₄SCN solution.⁶ The cathodic polarization curves reported so far for the NH₄SCN solution⁶,⁷ have shown that the reactions on the high potential side overlap the anodic reaction of iron; they have not yielded sufficient information about the cathodic reactions, including those in Eqs. (2) and (3), or the rates of reaction. Therefore, polarization measurements were conducted in an environment that inhibited the anodic reaction in order to confirm the cathodic reactions occurring in the NH₄SCN solution.

Figure 3 presents the cathodic polarization curves measured for a stable Pt working electrode in a NH₄SCN solution under the conditions described in subsection 2.5. Gas phase atmospheres of Ar deaeration and air were used to investigate the effect of dissolved oxygen, and a 20 mass% NH₄SCN aqueous solution and a 3 mass% NaCl aqueous solution were used as the test solutions to investigate the effect of NH₄SCN.

All the polarization curves show that the current increased from the immersion potential and a diffusion-limited current is observed near a potential of −0.3 V vs. SCE. Because the diffusion-limited current density was dependent on the Ar deaeration atmosphere regardless of whether or not NH₄SCN was used as the solution, it indicates the diffusion limitation of dissolved oxygen in Eq. (2). A comparison of the diffusion-limited current density in the deaeration atmosphere with that in the air atmosphere suggests that dissolved oxygen declined by more than 90% in the former atmosphere compared with the latter.

The increase seen in the cathodic current density in a less noble potential region of −0.7 vs. SCE in the 3 mass% NaCl aqueous solution was probably due to a reduction reaction involving water shown in Eq. (4).

\[ \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  

(4)

The increase in the current density observed in a less noble potential region of −0.5 V vs. SCE in the NH₄SCN aqueous solution is presumably ascribable mainly to the cathodic reaction in Eq. (3) involving NH₄SCN.

Based on the cathodic reactions at the Pt electrode shown in Fig. 3, it can be concluded that the principal cathodic reactions in the NH₄SCN aqueous solution environment were the reduction reaction of dissolved oxygen in Eq. (2), the reaction in Eq. (3) involving NH₄SCN, and the cathodic reaction in Eq. (4), which occurred in that order from the noble potential region.

Figure 4 shows the polarization curves measured for the steel working electrode in a NH₄SCN solution concentration of 0, 0.5, 2 and 20 mass%. Measurements were made in an Ar deaeration atmosphere under the conditions described in subsection 2.5. The polarization curves for the 0 and 0.5 mass% NH₄SCN solutions are for cathodic polarization only. A 3 mass% NaCl solution was used in the case of the NH₄SCN concentration of 0%.

The current densities of the cathodic and anodic reactions declined with decreasing NH₄SCN solution concentration. The cathodic polarization curves measured for the 0.5, 2 and 20 mass% NH₄SCN concentrations show a change in slope near a potential of −0.9 V vs. SCE. The polarization curves obtained with the 3 mass% NaCl solution and with the solution containing NH₄SCN cannot be compared directly because the pH of the solutions differed. Taking into account the Ar deaeration atmosphere, it is assumed that the reaction in Eq. (3) involving NH₄SCN dominates in the region from the immersion potential to −0.9 V vs. SCE and that the cathodic reaction in Eq. (4) dominates in the region lower than the potential.

The influence of supply limitation on the NH₄SCN reacting interface was investigated in an immersion environment with solution flow. Figure 5 shows the polarization curves measured in the still and stirred NH₄SCN baths under the conditions described in subsection 2.5. A diffusion-limited current is not seen in the results for the stirred bath from a potential of −0.8 to −1.1 V vs. SCE, and the current density is also approximately 50% higher than that for the still bath in a potential region of −0.8 V vs. SCE. The current density increased exponentially relative to the change in potential in the stirred bath. Moreover, an inflection point is seen in the cathodic polarization curve in the still bath near a potential of −0.9 V vs. SCE tended to be the limiting factor. These results imply that the reaction in Eq. (3) shows the supply limitation of NH₄SCN in the still bath even for the 20 mass% concentration.

Table 3 shows the hydrogen content and weight loss due to corrosion of steel specimens following a 24-h immersion test conducted under the same conditions as for the specimens in Fig. 5. The weight loss due to corrosion increased in the stirred bath as would be inferred from the polarization behavior shown in Fig. 5. The hydrogen content of the steel specimens, on the other hand, declined in the stirred bath. That is presumably attributable to a decrease in hydrogen adsorption sites in a stirred solution environment and to the effect of the dissolution of steel that had absorbed hydrogen.

The solution concentration, NH₄SCN consumption by corrosion and the effect of solution flow were investigated as factors that might influence the supply of NH₄SCN to the steel surface. Hydrogen embrittlement tests conducted with a 20 mass% NH₄SCN solution confirmed that the consumption of about 2 mass% of NH₄SCN during the test did not have any effect on the time to rupture. The cathodic reaction in Eq. (3) involved in hydrogen absorption was not affected by dissolved oxygen concentration, but the rate of NH₄SCN supply to the steel surface. In hydrogen embrittlement tests using a 20 mass% NH₄SCN solution, solution flow induced by stirring might affect the time to rupture.

3.2. Effect of the Solution Temperature on Hydrogen Absorption

The relationship between the time to rupture t₀ (h) and the solution temperature T (K) in hydrogen embrittlement tests conducted under the same conditions as those in Fig. 1 is shown in Eq. (5) below for a tempered martensitic steel having a chemical composition close to that of the steel tested in this study.³

\[ t_0 = 2 \times 10^9 \cdot T^{-3.326} \]  

(5)

It was found from Eq. (5) that a 1°C difference in the solution temperature at 50°C had approximately a 7% effect on the time to rupture.

The hydrogen diffusion constant was measured at various solution temperatures using the hydrogen desorption method described in subsection 2.4 in order to investigate
Fig. 3. Cathodic polarization curves at the Pt electrode in the FIP test environment. Test conditions were atmospheres of air and Ar deaeration, solutions of 20 mass% NH$_4$SCN and 3 mass% NaCl, 50°C, static bath, SCE reference electrode and scan rate of 20 mV/min.

Fig. 4. Effect of solution concentration on polarization behavior of tested steel. Test solutions used were 0, 0.5, 2 and 20 mass% NH$_4$SCN and 3 mass% NaCl. Test conditions were 50°C, Ar deaeration atmosphere and still bath.

Fig. 5. Effect of solution flow on polarization behavior of tested steel. Flow was generated by stirring the solution with a magnetic stirrer. Test conditions were a 20 mass% NH$_4$SCN aqueous solution, 50°C and Ar deaeration atmosphere.

Fig. 6. Estimated hydrogen equilibrium concentrations in the initial period of the FIP test using the hydrogen diffusion coefficient. Test conditions were a 20 mass% NH$_4$SCN solution and solution temperatures of 30, 50 and 70°C. (1) Hydrogen diffusion coefficients calculated from hydrogen desorption and (2) hydrogen equilibrium concentrations estimated based on the increase in the hydrogen content of the specimens.

Table 3. Effect of solution flow on weight loss and hydrogen content of the tested steel in immersion tests.

<table>
<thead>
<tr>
<th>Solution flow</th>
<th>Weight loss/g m$^{-2}$</th>
<th>Hydrogen concentration/mass ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Still</td>
<td>10.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Stirred</td>
<td>18.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>
the relationship between the solution temperature and the equilibrium concentration of hydrogen on the steel surface which influences hydrogen absorption. The apparent hydrogen diffusion coefficient was calculated based on the equation\(^9\) shown in Eq. (6) below for the diffusion of matter in an endless cylinder.

\[
\frac{H}{H_0} = 4 \sum_{\beta = 1}^{\infty} \beta \cdot \exp \left( -\beta^2 \cdot D \cdot t \cdot r^2 \right) \quad \ldots \ldots \quad (6)
\]

where \(H\) is the hydrogen content, \(H_0\) the initial hydrogen content, \(D\) the diffusion coefficient, \(r\) the radius of the test specimen, \(t\) the elapsed time, and \(\beta\) the zero-dimensional Bessel function of the \(n\)th term. The diffusion coefficient was calculated using Eq. (6) for hydrogen desorption and the values of \(H/H_0\) and \(t \cdot r^2\) obtained from the experimental results.\(^{10}\)

Figure 6(1) shows the hydrogen content of the steel specimens as a function of elapsed time during hydrogen desorption at solution temperatures of 30, 50, and 70°C. Because the analysis of the hydrogen content by TDA revealed that hydrogen desorption was completed at 200°C, it was inferred that the absorbed hydrogen was diffusive hydrogen. Under a condition of a high holding temperature, the hydrogen content of the specimens tended to decline earlier because hydrogen desorption from the steel was promoted. The hydrogen diffusion coefficients at each solution temperature of 30, 50, and 70°C are denoted in Fig. 6(1) as \(D_{30}, D_{50}\), and \(D_{70}\), respectively. The values are approximately three orders of magnitude smaller than the hydrogen diffusion coefficient of \(\alpha\)-Fe,\(^{11}\) but they agree well with the hydrogen diffusion coefficient of approximately \(10^{-11}\) m s\(^{-1}\) that was found for the same type of tempered martensitic PC steel at room temperature by the hydrogen permeation method.\(^{12}\)

The activation energy for hydrogen diffusion \(E_D\) was 52.7 kJ mol\(^{-1}\). The hydrogen diffusion coefficients thus found were used to calculate the decay curves of the hydrogen content of the specimens with Eq. (6). The curves shown in the figure agree for the most part with the experimental results. The slight divergence from the hydrogen content at time 0 occurred because the calculation term of the infinite series in Eq. (6) was set as high as \(n = 10\).

The equilibrium concentration of hydrogen on the steel surface in the initial immersion period when the hydrogen content of the specimens was increasing was found with Eq. (7) below. This equation was obtained by modifying Eq. (6) for hydrogen absorption under the assumption that the effect of hydrogen desorption was small.

\[
\frac{H}{H_\infty} = 1 - 4 \sum_{\beta = 1}^{\infty} \beta \cdot \exp \left( -\beta^2 \cdot D \cdot t \cdot r^2 \right) \quad \ldots \ldots \quad (7)
\]

where \(H_\infty\) is the saturated hydrogen content for infinite time. Using the \(D_{30}, D_{50}\), and \(D_{70}\) diffusion coefficients, Eq. (7) was fitted to the changes in the hydrogen content of the specimens from the initial immersion period with elapsed time, and the equilibrium concentration of hydrogen at which the hydrogen content of the steel saturated was calculated. The results are shown in Fig. 6(2). The experimental data for the increase in the hydrogen content of the specimens all show good agreement with the calculated values. The equilibrium concentration of hydrogen on the steel surface at which the hydrogen content saturated increased only slightly from 7 to 7.5 ppm as the solution temperature was raised from 30°C to 70°C.

Figure 7 shows the polarization curves measured for different solution temperatures under the conditions described in subsection 2.5. Both the anodic and cathodic polarization curves indicate that the reactions were promoted as the solution temperature was increased. A comparison of the results in the region of a potential of \(-0.75\) V vs. SCE in particular, which corresponds to the reaction in Eq. (3), shows that the current density at 70°C was approximately 30 times greater than that at 30°C.

Steels with a high dislocation density like tempered martensitic PC steel show a decline in the equilibrium concentration of hydrogen on the steel surface at high temperatures because of the promotion of hydrogen desorption such as the behavior seen in Fig. 6(1). The reason why the equilibrium concentration of hydrogen on the specimen surface was maintained under the immersion conditions in Fig. 6(2) for different solution temperatures was probably because the reaction in Eq. (3) was promoted to a greater extent than hydrogen desorption. As a result, the equilibrium concentration of hydrogen remained virtually constant regardless of the solution temperature.

The time when the calculated equilibrium concentrations of hydrogen began to diverge greatly from the experimental results was in the vicinity of the maximum hydrogen content as seen in Fig. 6(2). Because the corrosion film had a small effect on hydrogen desorption, the changes in the equilibrium concentration of hydrogen might signify a decline or a change in the reaction in Eq. (3) with elapsed time.

The corrosion current density was calculated from the
polarization curves in Fig. 7. The apparent activation energy for corrosion of the steel specimens was 49 kJ mol\(^{-1}\) in a solution temperature range from 30 to 70°C, 48 kJ mol\(^{-1}\) from 30 to 50°C, and 51 kJ mol\(^{-1}\) from 50 to 70°C. Because nearly the same values were obtained, it is assumed that the corrosion reaction mechanism did not change in the solution temperature range from 30°C to 70°C.

The change in the corrosion rate with elapsed time during the immersion test was measured in terms of the polarization resistance, a time history of which is shown in Fig. 8. The test environment was a 20 mass% NH\(_4\)SCN solution at 50°C and an air atmosphere, the same as the conditions in Fig. 6. Measurements were made in a polarization range of the spontaneous potential \(\pm 15\) mV and at a sweep rate of 10 mV min\(^{-1}\). The corrosion rate \(R_p\) corresponds to the reciprocal of polarization resistance. The results show that the corrosion rate declined with elapsed time. The corrosion rate declined significantly after 24 h, the time at which the calculated equilibrium concentrations of hydrogen began to diverge from the experimental results in Fig. 6(2). As a result, the hydrogen absorption rate decreased, and owing to the balance with the rate of hydrogen desorption from the steel specimens, the hydrogen content in the steel presumably displayed its maximum level at an elapsed time of 24 h. Conceivable reasons for the decline in the corrosion rate include a reduction of the adsorption area of atomic hydrogen or a reduction of the rate of the reaction in Eq. (3) owing to an increase in the solution pH or the formation of a corrosion film on the steel surface.

Because the reaction in Eq. (3) continued at a reduced rate after the hydrogen content reached its peak level, a Fe(OH)\(_3\) sediment formed from iron (III) ions continued to precipitate at the outer layer of the corrosion film. The structure of the corrosion film that formed had a high concentration of S in its inner layer and a high concentration of O in its outer layer.4,6)

3.3. Change in Solution pH during Polarization Measurement

Table 4 shows the change in the pH of the test solution near the counter electrode before and after the polarization measurements in Figs. 4 and 5. The changes in the pH of the solution shown in Table 4 were affected by the electric charge at the time of the polarization measurement and by the solution flow when the solution was sampled. Consequently, the absolute values of these changes in pH are not quantitative. However, the direction of the change in pH, either increasing or decreasing, can be seen from the results. After the anodic polarization measurement, the pH of the test solution tended to be higher near the Pt counter electrode in both the stirred and still baths. After the cathodic polarization measurement, on the other hand, the pH of the test solution near the Pt electrode decreased in the still bath, but was virtually unchanged in the stirred bath. Similar pH change might occur during electrolytic hydrogen charging in a solution containing NH\(_4\)SCN. The cause of the pH change was investigated because the phenomena might be related to reactions that occur when a steel specimen is immersed in a NH\(_4\)SCN solution. It is possible that these same phenomena might also occur during electrolytic hydrogen charging in a solution containing NH\(_4\)SCN regardless of the concentration. The cause was investigated because the phenomena might be related to reactions that occur when steel specimen is immersed in a NH\(_4\)SCN solution.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Flow</th>
<th>Polarization*</th>
<th>(\Delta) pH**</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 mass% NH(_4)SCN</td>
<td>Still</td>
<td>Anode</td>
<td>+1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cathode</td>
<td>−0.9</td>
</tr>
<tr>
<td>2 mass% NH(_4)SCN</td>
<td>Still</td>
<td>Anode</td>
<td>+0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cathode</td>
<td>−0.5</td>
</tr>
<tr>
<td>0.5 mass% NH(_4)SCN</td>
<td>Still</td>
<td>Anode</td>
<td>+0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cathode</td>
<td>−0.4</td>
</tr>
<tr>
<td>20 mass% NH(_4)SCN</td>
<td>Stirred</td>
<td>Anode</td>
<td>+1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cathode</td>
<td>−0.1</td>
</tr>
</tbody>
</table>

*Anode and cathode show the polarity of the working electrode of steel. A counter electrode is Pt.
**pH change at the polarization measurements.

Fig. 9. Change in pH of the test solution near the steel working electrode (WE) and that near the steel or Pt counter electrode (CE) during cathodic potentiostatic polarization tests. Test conditions: 20 mass% NH\(_4\)SCN, 50°C, 2 h, still bath, air and the potential of WE \(-1.542\) V vs. SCE.
Figure 9 shows the changes measured in the pH of the test solution in each chamber of a glass separate chamber type electrochemical cell during potentiostatic polarization tests under the conditions described in subsection 2.6. A steel electrode was used in the cathode chamber, and steel and Pt electrodes were used in the anode chamber. It is seen that the pH of the test solution declined only in the anode chamber with a Pt electrode. Following the measurement, the solution and the electrode surface in the anode chamber with a Pt electrode where the pH declined turned yellow in color. An analysis of the solution in the anode chamber using an ion chromatography system detected 1,300 ppm of SO₄²⁻. H₂ was detected in the cathode chamber with the steel electrode.

The reaction at the steel electrode as the anode is shown in Eq. (1) and the pH of the solution there did not change. The reactions at the steel electrode acting as the cathode consisted of those in Eq. (3) and a simple proton reduction reaction, so the pH of the solution there increased. It is seen that the pH of the solution near the anode was always lower than that near the cathode. Presumably, that was due to the effect of diffusion of the high pH solution near the cathode through the porous glass.

In the case of a Pt anode, oxidation of the large quantity of SCN⁻ ions present in the solution can be cited as a reaction that produces SO₄²⁻. The standard electrode potential E° for SCN⁻ is shown in Eq. (8). (14)

$$\text{(SCN)}_2 + 2e \rightarrow 2\text{SCN}^- \quad E^o = +0.77 \text{ V vs SHE} \ldots \quad (8)$$

E° in Eq. (8) shows that SCN⁻ tends to oxidize at the Pt electrode and (SCN)₂ may be produced. (SCN)₂ is unstable in an aqueous solution and acts on water as a strong oxidant, quickly promoting hydrolysis to produce SO₄²⁻ ions. (15) In addition, the hydrolysis of S²⁻ ions produced by the cathodic reaction in Eq. (3) at the steel electrode forms HS⁻ ions, which might be oxidized in the vicinity of the Pt electrode as the anode to form SO₄²⁻ and S⁰ as well.

Many different reactions have been reported as ones that occur between NH₄SCN and the resultant SO₄²⁻, including one that produces a yellow sediment, expressed in chemical formula as C₂H₂N₂S₃, and which is not accompanied by the generation of any gas. (16)

During electrolytic hydrogen charging and polarization measurement in a NH₄SCN solution, the production of SO₄²⁻ originating from the oxidation of SCN⁻ at the Pt electrode serving as the anode might cause the pH of the solution to decline. At the steel electrode acting as the cathode, the hydrogen generation reaction containing the reaction in Eq. (3), the same one that occurs during the immersion test in a NH₄SCN solution, induces hydrogen absorption. On the other hand, the pH of the solution rises due to the proton consumption reaction in Eq. (3).

4. Conclusions

This study investigated the effects of the immersion conditions on the time to rupture of tempered martensitic PC steel in the FIP test and on the formation reaction of a corrosion film in a NH₄SCN solution environment. The following insights were gained from the experimental results.

1. The activation energy for hydrogen diffusion E_D in the steel tested in this study was found to be 52.7 kJ mol⁻¹ based on hydrogen desorption that occurred in a solution temperature range from 30°C to 70°C.

2. The decline in the NH₄SCN concentration due to consumption of NH₄SCN was found to have a negligible effect on the time to rupture in the FIP test.

3. A supply limitation was observed for a still bath of a 20 mass% NH₄SCN solution. Stirring the bath promoted the formation of a corrosion film and suppressed hydrogen absorption, indicating that solution flow might affect the time to rupture in the FIP test.

4. The NH₄SCN concentration was found to have a large effect on hydrogen absorption, but the effect of dissolved oxygen was small. It is inferred that an iron sulfide film has a greater effect on suppressing hydrogen absorption than an iron oxide film.

5. The equilibrium concentration of hydrogen on the steel surface was maintained at 7.1–7.4 mass ppm in the process where the hydrogen content of the steel increased in a solution temperature range from 30°C to 70°C.

6. The change in the hydrogen content of the tested steel with elapsed time in the FIP test environment with a solution temperature of 50°C was presumably determined by the balance between the decline in hydrogen absorption accompanying a reduction of the corrosion rate and the rate of hydrogen desorption.

7. In potentiostatic polarization tests conducted in a solution containing NH₄SCN it was observed that the formation of SO₄²⁻ near the insoluble Pt anode caused the pH of the solution to decline.

REFERENCES