Hydrogen Embrittlement Evaluation Methods for Ultra-high Strength Steel Sheets for Automobiles

Shusaku Takagi1), Yuki Toji2), Kohei Hasegawa2), Yasushi Tanaka3)
Norbert Rössler4), Brigitte Hammer4), Thomas Heller4)
1) JFE Steel Corp., 1, Kawasaki-cho, Chuo-ku, Chiba 260-0835, Japan (E-mail s-takagi@jfesteel.co.jp)
2) JFE Steel Corp., 1, Kokan-cho, Fukuyama, Hiroshima 721-8510, Japan
3) JFE Steel Corp., 1, Kawasaki-cho, Chuo-ku, Chiba 260-0835, Japan
4) Thyssen-Krupp Steel Europe AG, Kaiser-Wilhelm-Str. 100 47166 Duisburg, Germany

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In order to apply ultra-high strength steel sheets with tensile strength of 980MPa or higher to automobiles, it is necessary to ensure the safety of steel parts against hydrogen embrittlement (HE). HE is influenced by hydrogen content and stress and strain introduced in parts by various forming processes. In this paper, the critical HE conditions for 1180MPa grade steels were investigated with specimens formed by bending and drawing. The critical hydrogen contents of the HE regions induced by both forming modes decreased with increasing equivalent strain. The critical HE conditions were also compared.

Key words: materials, high-strength steel sheet, fracture / Hydrogen embrittlement, U-Bending, Drawing, Equivalent strain (D3)

1. INTRODUCTION

Application of ultra-high strength steel sheets with tensile strength of 980MPa or higher to automobiles with the aim of reducing body weight has increased by the year(1). It is well known that hydrogen embrittlement susceptibility becomes larger as the strength of steel increases(2-4). The risk of hydrogen embrittlement (HE) should be evaluated before using parts made of ultra-high strength steel sheets in car bodies(5,6). Automotive parts are formed by various working processes such as bending, drawing and stretch forming. Therefore, HE fracture conditions should be assessed under these forming methods. However, the effects of the forming mode on HE conditions have not been clarified. In this study, the HE conditions of ultra-high strength steels with tensile strength of 1180MPa grade were investigated after formed by two methods in order to examine the effects of the forming mode on the HE region.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

1180MPa grade cold-rolled dual-phase (ferrite-martensite) steel (1180DP)(1) and hot-rolled martensitic steel (MS-W 1200)(7) were used. The microstructures are shown in Figure1. The thickness of the 1180DP was 1.6mm, and that of the MS-W 1200 was 1.5mm.

2.2. Methods of evaluating hydrogen embrittlement

HE properties were evaluated by two methods, as described below. In each method, the specimens were immersed in HCl solutions of various pH from 1 to 4 or a NaCl solution of pH 7.

(1) U-bend method(5,6)

Materials were sheared parallel or transverse to the rolling direction, and the sheared edges were ground. In this paper, the former specimens are called L direction specimen and the latter are called T direction specimen. The specimens were bent with various radiuses, and only the conditions under which all specimens did not fracture for 96hr were judged as the unfracture condition. The stress in the longitudinal direction of the specimens at the outside surface of the
top was measured by X-ray diffraction (XRD) method. Equivalent strain at the surface was calculated using Eq. 1.

\[ \varepsilon_{eq} = \varepsilon/(2R + t) \times 2/\sqrt{3} \] (1)

where \( R \) the bending radius and \( t \) the thickness of the steel sheet.

(2) Drawn cup method

Materials were drawn with drawing ratios from 1.3 to 2.0. The cup diameter was 50mm, and the lubricant used during drawing was a polypropylene sheet or oil. The edge of the blank was machined before drawing. The cup rim after drawing was as-formed. The test was conducted with two or more cups for each drawing ratio, and the conditions under which all cups did not fracture for 90hr were judged as the unfracture condition. Equivalent strain was calculated by Finite Element Analysis in which the conditions were defined as yield strength of L direction, yield criterion of von Mises model, work hardening model of a combination of Swift and Voce equations(8) and r-value of 1 as anistropic parameter. In the work hardening model, parameter \( \alpha \) as a liner combination factor was determined for each material at 0.297 for 1180DP and 0.356 for MS-W1200. Residual stress in the tangential direction was measured by XRD from near the surface to the center of thickness of the specimens. The specimens were etched electrolytically to the intended measurement points in order to measure the stress at various points in the thickness direction.

2.3. Hydrogen content analysis

The diffusible hydrogen content penetrating the specimens was measured by Thermal Desorption Analysis (TDA) with JTA20A System made by J-SCIENCE LAB Co.,Ltd. The hydrogen detector was gas chromatography. With the cup specimens, samples approximately 5mm in width and 30mm in length were cut from the cup rim, as shown in Figure 3. With the U-bend specimens, samples of approximately the same size as with the cup specimens were cut from the top of the specimens. The heating rate in TDA was 200K/hr. The hydrogen content up to 573K, which was the end of the first peak of the hydrogen evolution curve, was defined as diffusible hydrogen. The peak temperatures of all specimens were almost the same as about 423K.

3. EXPERIMENTAL RESULT

3.1. Mechanical properties of test steels

The mechanical properties of the test steels are shown in Table 1. Bending limit means the minimum bending radius to which the material could be bent without cracking. The good elongation and bendability of 1180DP are attributed to its dual-phase microstructure. MS-W 1200 showed good stretch flangeability, which was attributed to its uniform martensitic microstructure.

![Fig. 2 Preparation of test piece for U-bend hydrogen embrittlement test.](image1)

![Fig. 3 Sampling position of a sample for TDA and measurement point of residual stress in cup specimen.](image2)

*\( a \): Cup height (7 ~ 38mm, depending on drawing ratio)

*\( b \): Measurement position of residual stress in thickness direction

![Table 1 Mechanical properties of steels used.](image3)

| Materials     | Direction | YP / MPa | TS / MPa | EL(%) | \( \lambda \) (%) | Bending limit / mm |
|---------------|-----------|----------|----------|-------|------------------|-------------------|
| 1180DP        | L         | 906      | 1214     | 14.5  | 40               | 2.0               |
|               | T         | 897      | 1233     | 13.7  |                  | 3.0               |
| MS-W1200      | L         | 1075     | 1284     | 6.3   | 66               | 5.0               |
|               | T         | 993      | 1229     | 6.8   |                  | 5.0               |

*\( \lambda \): Hole expanding ratio

![Fig. 4 Relationship between bending radius and equivalent strain at top of U-bend specimens with thickness of 1.6mm.](image4)

3.2. Hydrogen embrittlement evaluation results

(1) U-bend method

The critical conditions for HE are considered to be influenced by stress, strain, and diffusible hydrogen content. First, the influences of these factors were investigated for both materials.

Figure 4 shows the relationship between the bending radius and equivalent strain calculated with Eq.1, which is one candidate as a factor in fracture. The equivalent strains increase from 0.09 to 0.24 corresponding to the decrease of the bending radiiuses from 10mm to 3mm. The stresses of the U-bend specimens were 900MPa for 1180DP and 700MPa for MS-W 1200, independent of the bending radius.
The effect of immersion time on the diffusible hydrogen content penetrating specimens is shown in Figure 5. The immersion solution was HCl of pH 3, and the bending radius was 5mm. The diffusible hydrogen content is substantially saturated after immersion for 48h, and the saturated diffusible hydrogen contents of both steels were virtually the same. Figure 6 shows the relationship between the bending radius and the diffusible hydrogen content in the top of the U-bend specimens of 1180DP immersed in HCl of pH 1 for 96h. The diffusible hydrogen content increased with decreasing bending radius, in other words, increasing equivalent strain. Figure 7 shows the influence of pH on the content of diffusible hydrogen penetrating the specimens of 1180DP. The content of diffusible hydrogen after immersion in the pH 1 solution was higher than with the pH 3 solution\(^9\). According to past studies, the diffusible hydrogen content attributable to the environment during service was estimated at around 0.1wt ppm\(^9\). Therefore, it is considered that the immersion test in HCl with pH 1 is quite severe compared with the actual environment.

Figure 8 shows the results of the HE test with the U-bend specimens. When L direction specimens of 1180DP were immersed in HCl of pH 1, the specimen with the bending radius of 3mm fractured. On the other hand, all T direction specimens fractured. However, when the T direction specimens were immersed in HCl of pH 3, only the specimen with the bending radius of 3mm fractured. Thus, with 1180DP, the L direction specimens had lower sensitivity for HE than the T direction specimens. With MS-W 1200, all L direction specimens fractured when immersed in HCl of pH 1, but with the T direction specimens, only those with the bending radius of 5mm fractured. In HCl of pH 3, only the L direction specimens with the bending radius of 5mm fractured.

With both steels, the critical bending radius was different in the L direction specimens and T direction specimens. With 1180DP, the L direction specimens were less susceptible to HE than the T direction specimens. However, with MS-W 1200, the less susceptible direction was the T direction. The more sensitive cases correspond to higher TS and lower El in tensile tests.

**Table 1**

| pH1 | L direction | pH1 | L direction |
|-----|-------------|-----|-------------|
| O   | O           | X   |             |

| pH3 | L direction | pH3 | L direction |
|-----|-------------|-----|-------------|
| O   | O           | X   |             |

| pH1 | T direction | pH1 | T direction |
|-----|-------------|-----|-------------|
| X   | X           | X   |             |

| pH3 | T direction | pH3 | T direction |
|-----|-------------|-----|-------------|
| O   | O           | X   |             |

**Figure 8** Results of hydrogen embrittlement tests with U-bend specimens of (a) 1180DP and (b) MS-W1200. O and X marks indicate unfracture and fracture conditions, respectively.

Under immersion in the pH 3 solution, which means that diffusible hydrogen of approximately 0.5wt ppm penetrates the steel with the bending radius of 5mm, it is predicted that HE will not occur except under deformation at the bending limit. Heavy deformation introduces many defects, which include point defect, dislocation, microvoid and microcrack in this paper, into materials, and those defects allow a large amount of diffusible hydrogen to penetrate the steels. The existence of those defects and the diffusible hydrogen tend to induce HE.

It is well known that HE sensitivity is improved by decreasing
applied stress\textsuperscript{(10,11)}. The same tendency was observed in the U-bend test. With 1180DP, HE did not occur in HCl of pH 3 under a lower stress condition of approximately 650MPa, even under the severest bending radius condition.

With the U-bend method, the safe region of 1180DP was slightly wider than that of MS-W 1200.

(2) Drawn cup method

In drawn cup tests, fracture occurs at the cup rim. Figure 9 shows the relationship between the drawing ratio and the equivalent strain at the rim with 1180DP. Equivalent strain increases as the drawing ratio increases. The relationship between the drawing ratio and equivalent strain at the rim with MS-W 1200 was almost the same as with 1180DP. Equivalent strain can be changed more widely by drawing than by bending. Figure 10 shows the distribution of the tangential residual stress at the surface of specimens from the bottom to the rim. The stress near the rim was lower than that near the bottom of the specimen. In spite of this stress distribution, the cup specimens fractured from the rim edge. Figure 11 shows the distribution of tangential stress in the cup thickness direction with a drawing ratio of 2 at a position 30mm from the bottom of the specimen. Maximum stress was approximately 900MPa, and the maximum stress point was 0.4mm from the surface. It is considered that cup specimens fracture from the rim as a result of this internal tensile residual stress. With MS-W 1200, the residual stress distribution of the cup with the drawing ratio of 2 was almost the same as with 1180DP. With 1180DP, the cup with the drawing ratio of 1.6 had substantially the same stress distribution as with that of the drawing ratio of 2 along the thickness near the rim. Figure 12 shows the relationship between the drawing ratio and the diffusible hydrogen content near the rim for 1180DP. The diffusible hydrogen content increased as the drawing ratio increased. Figure 13 shows the results of the immersion tests of the cup specimens using HCl or NaCl solutions. With 1180DP, the critical drawing ratios in solutions of pH 1, pH 3 and pH 7 were 1.3, 1.4 and 1.6, respectively. Those with MS-W 1200 were 1.7, 1.8 and 1.9, respectively. Thus, the critical drawing ratios for HE became larger with increasing pH.

With the drawn cup method, the safe region of MS-W 1200 was wider than that of 1180DP. The reason why the safe region of the materials varies depending on the evaluation method is considered to be because the effects of the forming method on the number and/or nature of defects introduced into the material during forming are
different, depending on the material.

4. DISCUSSION

A new delayed fracture evaluation concept was suggested by Y. Toji et al\(^5\). In this concept, first, the HE region is indicated on a 3-dimensional diagram of stress, strain and diffusible hydrogen content. Next, the conditions of actual parts are compared with the HE region. Actual parts are formed by various forming modes. Therefore, if the HE conditions are substantially the same, independent of the forming mode, the risk of HE of the parts can be predicted using only one diagram prepared for one forming mode. In this chapter, the HE regions acquired with the U-bend test and drawn cup test are compared with the 3-dimensional diagram, and the possibility of predicting the risk of HE with only one diagram is discussed.

In order to compare the HE conditions of the two forming modes, each HE condition must be indicated by stress, strain and diffusible hydrogen content at the fracture initiation point. In the U-bend test, the fracture initiation point is at the top of the specimen. The stress factor was evaluated using the stress in the longitudinal direction of the specimen measured by the XRD. The strain factor can be calculated by bending theory. It is considered that the strain factor is an index of defects which are thought to promote HE. In this paper, equivalent strain was applied as the strain factor.

As the diffusible hydrogen factor, the diffusible hydrogen contents at the surface of the specimens were derived as described in the following. In U-bend specimens, a hydrogen content distribution exists in the thickness direction. The hydrogen content measured by TDA is the average hydrogen content in the specimen. The hydrogen content at the surface can be estimated from the relationship between the saturated diffusible hydrogen content, which means the hydrogen content which penetrated the specimen during immersion in a solution for 96h, and the equivalent strain.

Figure 14 shows the relationship between the diffusible hydrogen content and equivalent strain for 1180DP, in which strain was applied by rolling or tension, with immersion in HCl of pH 3 for 96h\(^{12}\). The diffusible hydrogen content and equivalent strain showed the same relationship, independent of the deformation mode. Figure 15 shows an example of the diffusible hydrogen contents at the surfaces of U-bend specimens estimated from the data in Fig. 14 and Fig. 4. The hydrogen contents at the surface were higher than the average contents. Hydrogen contents at fracture times shorter than 96h are not applicable for the HE evaluation in this paper because the hydrogen content may not yet be saturated, which means that the relationship between the measured hydrogen content and the hydrogen content at the surface is not clear. When the fracture data were plotted, the saturated hydrogen contents of the specimens immersed continuously until 96h were used, even if the specimens fractured earlier.

In the drawn cup test, the fracture initiation point is situated at the cup rim of the specimen. The maximum tangential stress near the rim measured by XRD was applied as the stress factor. The maximum stress point is located 0.4mm from the surface, as shown...
in Figure 11. As the strain factor, the equivalent strain at the rim edge calculated by FE analysis was used. As the diffusible hydrogen factor, the hydrogen contents were measured with samples cut from the rim edge, as shown in Fig. 3. Because the strain distribution in the thickness direction is small, the hydrogen content is assumed to be uniform.

The HE regions for 1180DP were compared in a 2-dimensional diagram of the equivalent strain and the diffusible hydrogen content because the stresses with both test methods applied to 1180DP were almost the same as those with 900MPa. In the cup test, the specimens fractured at various positions on the rim, not only in the rolling direction but also the transverse or the diagonal direction. Fracture initiation was most frequent in the diagonal and rolling directions. Therefore, the HE region obtained with the U-bend tests of transverse direction specimens in which cracks occurred in the rolling direction were used in the comparison with the HE region obtained with the drawn cup test.

Figure 16 shows the results of the comparison of the HE regions obtained by the two methods. With both methods, the critical hydrogen contents of the HE regions decreased with increasing equivalent strains. However, the critical HE condition obtained with the drawn cup test is located in a higher hydrogen content and larger equivalent strain area than that obtained in the U-bend test. The reason for this difference is conjectured to be that equivalent strain was not adequate as an index of the defects introduced into the materials during forming. If the criterion for evaluating defects is selected properly, it is expected that the critical condition for HE can be determined identically, independent of forming mode. In future work, the critical conditions of HE for other types of materials, for example MS-W 1200, will be compared, and effective use of this new concept as an HE evaluation method will be investigated.

5. CONCLUSION

In order to promote the application of ultra-high strength steel sheets to automobiles, the critical conditions of hydrogen embrittlement for 1180MPa grade dual-phase steel (1180DP) and martensitic steel (MS-W 1200) were investigated by two methods, i.e., the U-bend test and the drawn cup test. In the U-bend test, the safe region to avoid hydrogen embrittlement of 1180DP was wider than that of MS-W 1200. On the other hand, in the drawn cup test, the safe region of MS-W 1200 was wider. With 1180DP, the critical hydrogen content of the HE region decreased with increasing equivalent strain with both test methods. The critical hydrogen embrittlement conditions obtained by the two methods showed a difference in the two dimensional diagram for constant stress, in which the axes were stress, equivalent strain and diffusible hydrogen content. It is expected that the critical condition for HE can be

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