Hydrogen Embrittlement Resistance Evaluation of Ultra High Strength Steel Sheets for Automobiles

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1. Background

Ultra high strength steel (UHSS) sheets with tensile strength over 980 MPa have been applied to automobiles.1) The most well-known automotive parts using UHSS sheets are door impact beams and bumper reinforcements. The door impact beam is built into the door to prevent penetration of the other car in a side-impact collision. Application of UHSS sheets to many another automotive body parts has also been attempted in order to achieve further weight reduction, for example, in pillar reinforcements and member reinforcements.

When UHSS sheets with tensile strength over 980 MPa are applied in automobiles, there is a risk that a type of hydrogen embrittlement fracture called delayed fracture may occur while a vehicle is in use. This paper summarizes the effects of stress, strain, diffusible hydrogen content and the forming mode on the hydrogen embrittlement resistance of UHSS sheets for automotive applications. In this study, 1,180 MPa grade ferrite-martensite dual phase steel was used. This material was evaluated by the U-bending and drawn cup methods. It was concluded that high strain, high stress and high diffusible hydrogen content reduced hydrogen embrittlement resistance.

In addition, an improved immersion-type hydrogen charging method using an ammonium thiocyanate (NH4SCN) aqueous solution was introduced in this paper. The NH4SCN solution enables control of the diffusible hydrogen content from low to high concentrations using the NH4SCN concentration, and dissolution of the specimens during immersion in NH4SCN was minimal, making it possible to maintain substantially the same surface condition as before immersion.

KEY WORDS: delayed fracture; equivalent strain; equivalent stress; diffusible hydrogen; U-bending; drawn cup; ammonium thiocyanate; immersion-type hydrogen charging method.

2. Concept of Hydrogen Embrittlement Fracture Evaluation of Automotive UHSS Sheets

First, the aim of hydrogen embrittlement evaluation of automotive UHSS sheets will be explained. The controlling factors in hydrogen embrittlement fracture of HSS bolts are stress, diffusible hydrogen content and material characteristics, for example, material strength, microstructures and applied strain. For automotive UHSS sheets, applied strain should be considered as an important factor in hydrogen embrittlement fracture because material characteristics of UHSS sheets in the automotive part are influenced by strain introduced with forming. Therefore, our group suggested a 3-dimensional map concept for evaluating the risk of hydrogen embrittlement fracture of automotive parts. Figure 1 shows a schematic representation of the 3-dimensional map. The hydrogen embrittlement region is obtained on a 3-dimensional map with stress, strain and diffusible hydrogen content as its axes. If the combination of these three factors in a part is located in the cracking region, it is predicted that the part will fracture due to hydrogen embrittlement. Safe parts, which are not susceptible to hydrogen embrittlement, can be manufactured if the combination of factors is controlled to be outside the cracking region in this map.

3. Methods of Evaluating Hydrogen Embrittlement Resistance of Automotive UHSS Sheets

This chapter introduces methods of evaluating hydrogen
embrittlement in steel sheets. Table 1 shows studies concerning the evaluation of hydrogen embrittlement properties in UHSS sheets.\textsuperscript{4,5,8,12–20}

The most widely-used evaluation method for UHSS sheets is the U-bending method. This method is used because UHSS sheets are generally applied to door impact beams and bumper reinforcements, which are mainly formed by bending. Figure 2 shows an example of the procedure for preparing U-bending specimens. Rectangular specimens are sheared or punched from a steel sheet. Generally, the edges of the specimens are ground to remove the part damaged by shearing. Circular specimens are punched to various diameters corresponding to the drawing ratio of the specimen. Sample for hydrogen analysis are cut from the rim of the test piece, as shown in Fig. 3 (right).

The Constant Loading Test (CLT),\textsuperscript{22,23} Slow Strain Rate Technique (SSRT)\textsuperscript{24} and Conventional Strain Rate Test (CSRT),\textsuperscript{25–27} which are major evaluation methods in the field of UHSS bolts, have been minor methods in the field.
of UHSS sheets. Presumably, these methods are not widely used with UHSS sheets because only uniaxial deformation test can be conducted by those methods and it is more difficult to predict the risk of hydrogen embrittlement fracture in actual parts with considering the influence of forming modes. On the other hand, CLT, SSRT and CSRT have the advantage of enabling easy measurement of stress, strain and diffusible hydrogen content. Thus, if the above-mentioned problem can be solved, these may also become major methods for evaluating hydrogen embrittlement resistance in sheet steels.

4. Evaluation Results of Hydrogen Embrittlement Resistance of Automotive UHSS Sheets

This chapter introduces the results of some researches on the influences of various factors on the hydrogen embrittlement resistance of automotive UHSS sheets.

4.1. Effects of Stress, Strain and Diffusible Hydrogen Content on Hydrogen Embrittlement Resistance of 1 180 MPa Grade Dual Phase Steel Evaluated by U-bend Test

The hydrogen embrittlement resistance of 1 180 MPa grade dual phase steel (1180DP) with a thickness of 1.6 mm was evaluated. The microstructure and mechanical properties of 1180DP are shown in Fig. 4 and Table 2, respectively. U-bending specimens controlled to various bending radii and applied stresses were immersed in an HCl solution with pH 1 or pH 3 at 298 K. The conditions under which one or more specimen cracked within 96 hr were judged as the cracking condition. Figure 5 shows the hydrogen cracking region for bending radius and applied stress under the two pH conditions. In both cases, hydrogen cracking occurred in the regions of high stress and high strain corresponding to a small bending radius. However, the cracking region of the specimens immersed in HCl with pH 1 was wider than that with pH 3 because the content of diffusible hydrogen entering the specimens increased as pH decreases, as shown in Fig. 6. Figure 7 shows the influence of bending radius on the diffusible hydrogen content entering specimens immersed in a pH 3 HCl solution. Diffusible hydrogen content increased with decreasing bending radius, in other words, with increasing strain, as confirmed by the following experiment. Figure 8 shows the relationship between diffusible hydrogen content and equivalent strain. Strain was applied by rolling or tension with coupon samples of 1180DP, and the dependency of the diffusible hydrogen content on equivalent strain was confirmed.

From these results, it is concluded that high strain, high stress and high diffusible hydrogen content reduce hydrogen embrittlement resistance.

Table 2. Mechanical property of steel used.

<table>
<thead>
<tr>
<th></th>
<th>Yield Strength [MPa]</th>
<th>Tensile Strength [MPa]</th>
<th>Elongation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>906</td>
<td>1214</td>
<td>14.5</td>
</tr>
</tbody>
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Fig. 4. Microstructure of steel used (M: martensite, F: ferrite).

Fig. 5. Hydrogen cracking region of the investigated steel, (a) under pH 1 and (b) under pH 3 HCl.

Fig. 6. Influence of pH level of HCl and immersion time on the content of diffusible hydrogen entered the test pieces (R=5 mm).

Fig. 7. Influence of bending radius on the diffusible hydrogen content entering specimens in a pH 3 HCl solution.
embrittlement resistance.

4.2. 3-dimensional Map of Hydrogen Cracking Region of 1180DP

Figure 9 shows the hydrogen embrittlement region of 1180DP obtained from the U-bending test results on the 3-dimensional space of applied stress, applied strain and diffusible hydrogen content. An actual impact beam made of this steel, shown in Fig. 9, was located out of the hydrogen embrittlement region. Therefore, it is judged that the part is safe for hydrogen embrittlement.

4.3. Effect of Forming Mode on Hydrogen Embrittlement Resistance of UHSS Sheets

Actual parts for automobile are manufactured by various forming modes. If the hydrogen embrittlement resistances are substantially the same, independent of the forming mode, the risk of hydrogen embrittlement of these various parts can be predicted using only one 3-dimensional diagram acquired for one forming mode. However, the deformation mode may influence hydrogen embrittlement resistance. To investigate the influence of the deformation mode on hydrogen embrittlement resistance, a drawn cup test was conducted with the same 1180DP as above, and the hydrogen embrittlement regions in the drawn cup test and U-bending test were compared. The diameter of the drawn cup was a constant 50 mm, and the drawing ratio was changed from 1.2 to 2.0. The longest testing time was 96 hr which was the same as the U-bending method. In the region of these dimensions, stress was almost constant at around 900 MPa, independent of the drawing ratio. Therefore, the hydrogen embrittlement regions were compared under the applied stress of 900 MPa in the U-bend test and drawn cup test.

Figure 10 shows the results of a comparison of the hydrogen embrittlement regions obtained by the two methods. Stress, strain and diffusible hydrogen content were measured or estimated at the fracture initiation point, which is the surface of U-bending specimens and the rim of drawn cup specimens. With both test methods, the critical hydrogen content decreased with increasing equivalent strain. However, the critical hydrogen embrittlement (HE) condition obtained with the U-bending test was located in a lower hydrogen content and smaller equivalent strain area than that obtained with the drawn cup test. In other words, the U-bending test is a severer hydrogen embrittlement evaluation method than the drawn cup test. As one reason for this difference, it is conjectured that equivalent strain was not an...
adequate index of the defects introduced into the materials during forming. If the criterion for evaluating defects is selected properly, it is expected to be possible to obtain identical critical conditions for HE, independent of the forming mode.

5. Hydrogen Charging Method Using Ammonium Thiocyanate Solution

For evaluation of hydrogen embrittlement susceptibility, hydrogen must be charged into the specimens or parts. There are mainly three hydrogen charging methods, these being a cathodic charging method, immersion in an aqueous solution at free corrosion potential and exposure in an atmospheric corrosive environment. For hydrogen embrittlement evaluation of automotive steel sheets, it is necessary to test a large number of specimens in order to acquire a 3-dimensional map as described in this paper. In addition, actual parts should also be evaluated to confirm safety with respect to hydrogen embrittlement. Given these conditions, the immersion method is more convenient than the other methods, because many specimens can be easily and uniformly charged at the same time and large specimens with complex dimensions can be charged under uniform conditions. With the cathodic charging method, the current density distribution in a specimen depends on the specimen shape; in other words, it is considered that the hydrogen charging condition in a specimen changes depending on the local current density.

The immersion test also has the demerit that the specimens dissolve in the solution. This means that the surface conditions change during testing as a result of dissolution. To solve this problem, our group investigated an immersion-type hydrogen charging method with low dissolution of specimens.

The candidate was an ammonium thiocyanate (NH$_4$SCN) solution, which is well known for use in the Fédération Internationale de la Précontrainte (FIP) test for hydrogen embrittlement evaluation of bar steels and is also used as a catalyst for hydrogen charging. The effect of the concentration of the NH$_4$SCN solution on the diffusible hydrogen content and hydrogen embrittlement resistance was investigated.

Figure 11 shows the effect of the solution concentration on the diffusible hydrogen content entering U-bending specimens of 1180DP at 298 K. The diffusible hydrogen content increased with increasing concentrations of NH$_4$SCN solution. In the case of 1180DP, the diffusible hydrogen that entered the U-bending specimen during the immersion test with a 0.1% NH$_4$SCN solution was almost the same as that with immersion in a pH 1 HCl solution. Figure 12 shows the weight reduction during an immersion test in the NH$_4$SCN solution. The weight reduction with immersion in the NH$_4$SCN solution is significantly smaller than that with immersion in the HCl solution. For example, the weight reduction in a pH 1 HCl solution immersion test was 17%, but with the 0.1% NH$_4$SCN solution, weight reduction was only 0.08%. This is because the pH of the 0.1% NH$_4$SCN solution is 5.7, which is much higher than that of the pH 1 HCl. Figure 13 shows the specimen surface before and after immersion in the 0.1% NH$_4$SCN solution and pH 1 HCl. The change in the surface crack is minimal during immersion in the 0.1% NH$_4$SCN solution. If an NH$_4$SCN solution can be used appropriately, the immersion test can be conducted while maintaining virtually the same surface crack condition during the test. In the case of 1180DP, the hydrogen embrittlement region evaluated by immersing U-bending specimens in the NH$_4$SCN solution was almost the same as the region evaluated with an HCl solution, as shown in Table 3.
solution rate in this condition. Based on these results, the NH₄SCN solution can be used for evaluation of the hydrogen embrittlement resistance of UHSS sheets with low dissolution.

6. Summary

The hydrogen embrittlement resistance of automotive UHSS sheets was evaluated by various methods to support wider application of UHSS sheets. The effects of stress, strain, diffusible hydrogen content and the forming mode on hydrogen embrittlement resistance were investigated. A new immersion hydrogen charging method with low dissolution of specimens was also developed. The following results were obtained.

(1) Hydrogen embrittlement occurred more easily under high stress, high strain and high diffusible hydrogen content conditions.

(2) A 3-dimensional map concept for prediction of hydrogen embrittlement cracking was proposed, and a 3-dimensional map of 1180DP was acquired.

(3) The critical hydrogen embrittlement condition in U-bending was located in a lower hydrogen content and smaller equivalent strain area than that of the drawn cup specimens. In other words, under the same equivalent strain, the U-bending test was a severer evaluation method for hydrogen embrittlement resistance than the drawn cup test.

(4) Higher charging of diffusible hydrogen with lower specimen dissolution was possible by immersion in a NH₄SCN solution than in the conventional HCl solution.

7. Future Tasks for Evaluation of Hydrogen Embrittlement Resistance of Automotive UHSS Sheets

Many issues related to the evaluation of hydrogen embrittlement and delayed fracture in UHSS sheets for automotive applications still must be addressed. This chapter describes the main tasks for the future. First, the diffusible hydrogen content entering from various actual environments needs to be measured. These data are very important for improving the prediction accuracy of hydrogen embrittlement risk. Second, the effect of shearing or punching on hydrogen embrittlement resistance must be clarified. It is known that sheared or punched edges reduce hydrogen embrittlement resistance.7,17) Because sheet steels are always sheared or punched when manufacturing actual parts, it is very important to clarify the effect of sheared or punched edges on the hydrogen embrittlement resistance of UHSS sheets. Third, the effect of the forming mode on hydrogen embrittlement resistance requires further clarification. If a method of evaluating hydrogen embrittlement resistance independent of the forming mode is successfully developed, it will be possible to predict the hydrogen embrittlement risk of any part in the design stage. This would strongly encourage wider applications of UHSS sheets. The final task is an investigation of the effect of bake-hardening on hydrogen embrittlement resistance. Almost all steel sheets for automobiles are treated by the bake-hardening process. As shown in Fig. 14, the hydrogen entry into steels is suppressed by low-temperature treatments.29,30) This result means the content of hydrogen entering in steels is changed depending at time from forming of specimens to start of the hydrogen charging. Thus, for an accurate evaluation of the real risk of hydrogen embrittlement fracture in automotive steel sheets, it is important to clarify the effect of low-temperature treatment on hydrogen embrittlement resistance and the related mechanism.
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REFERENCES