Hydrogen Embrittlement of Ultrahigh-Strength Steels for Automotive Application: Risk Assessment and Mitigation

D. Cornette, S. Liu, A. Aouafi, S. Cobo, T. Dieudonné, T. Sturel

ArcelorMittal Global R&D, Voie Romaine BP 30320, 57283 Maizières-lès-Metz (France)
ArcelorMittal Global R&D, 3001 E. Columbus Drive East Chicago, IN 46312

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SUMMARY

Ultra-high strength steels (UHSS) show an increased susceptibility to hydrogen embrittlement compared to lower grades. It is well known that delayed failure is due to a combination of critical diffusible hydrogen contained in the material and an applied or residual mechanical stress for a given metallurgy. In this case, the quantity of hydrogen can be introduced during the steel manufacturing processes (annealing, coating deposition, ...) and / or car component processing (welding, phosphating, painting, and hot forming in the case of press hardened steel). Stress corrosion cracking (SCC) refers to a mechanism in which hydrogen is supplied by a corrosion attack.

Many tests have been developed by steel and carmakers to evaluate this sensitivity to delayed failure. These tests certainly allow to classify the various steels, but their nature (stress, hydrogen and acceleration over time) will not always allow to conclude the possibility of using safely the material.

In this paper, we give an overview of the different mechanical tests and medium generally used for the introduction of hydrogen. For new UHSS implementation, keeping the same acceptance criterion, as for the lower substituted grade, is not possible if not enough safety margin in the lab test exists because the critical level of diffusible hydrogen decreases when the tensile strength of the steel increases. As local diffusible hydrogen is difficult to quantify (cut edge, weld notch, scratch, corrosion), SCC tests are preferred instead of trying to position a critical level of diffusible hydrogen versus hydrogen coming from the environment.

Cyclic corrosion tests have been defined for corrosion status equivalency (in terms of material consumption) with natural exposure. To evaluate the representativeness of these accelerated tests, we try to link the hydrogen intake during these tests with the instantaneous corrosion rates. Threshold obtained on the different stress corrosion cracking tests can be used to evaluate the risk on car component by determining the level of applied stress with FEA.

INTRODUCTION

Susceptibility to hydrogen embrittlement (HE) is not a property of a material in the same sense as a mechanical property, but it is nevertheless a very important factor in determining the serviceability of metallic materials. The aim of HE testing is usually to provide information faster than it can be obtained from service experience, and at the same time, it attempts to predict service behavior. The most common approach employed to achieve this is the use of high stresses, slow continuous straining, higher concentration of species in the test environment than in the service one. In this framework, numerous tests exist for applying mechanical stress on samples to evaluate the risk of ultra-high-strength steel (UHSS):

- Slow strain rates tensile (SSRT) or constant load tests (CLT) on tensile specimen with or without hole or notches increasing the stress concentration factors (Kt) (Fig.1a).
- Bending tests also with maintained constraints including several support points (three points, four points...). It is used by many hot stampers and carmakers to evaluate the risk of delayed fracture for press hardened steels as it is considered as representative of the stresses on assembly parts on the body in white (Fig.1b).
- Tests on real parts, for which assembling efforts have been simulated by applying surrounding clamps (Fig.1c).
In the first part of this paper, two well-known and widely used delayed fracture tests in the automotive industry are applied for material approval of two ultra-high-strength steels, namely:

- SEP1970 test applied to MartInsite®1700 EG.
- Four-point bending test applied to PHS Usibor®2000 steel.

In the second part, two stress corrosion cracking tests, whose acceptance criteria have not yet been defined, are discussed, respectively:

- Step load test, according to VDA238-201, applied on several Zn-coated UHSS (980MPa<UTS<1800).
- Four-point bending test on Usibor®2000 in several corrosion conditions.

Finally, using a self-stressed laboratory specimen simulating all the stages of the automotive process and representative of an automotive component, we illustrate the good stress corrosion cracking behavior of our MartInsite®1700 EG and Usibor®2000-AS.

**DELAYED FRACTURE TEST TO ASSESS THE RISK ON THE MATERIAL AT DELIVERY CONDITION FOR COLD FORMING UHSS: EXAMPLE ON MARTINSITE®1700 EG.**

SEP1970 guidelines [1] define the testing conditions of AHSS for automotive against production-related hydrogen-induced brittle fracture. Among the two proposed tests, the most severe one, the tensile test with punched hole, has been selected. The main testing conditions are the following:

- Punching clearance of 10% for the center hole.
- Applied tensile load corresponding to 100% of the Yield Strength (nominal stress) of the material during the whole test duration.

The acceptance criterion is the four tested specimens free of cracks after 96h (4 days).

The results obtained on MartInsite® 1700 EG are summarized in the Table 1. The material is safe regarding these testing conditions thanks to a very low hydrogen content at delivery.

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>SEP 1970 (Testing Condition and Results)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature: 20°C</td>
</tr>
<tr>
<td></td>
<td>Shear edges (clearance 10%)</td>
</tr>
<tr>
<td></td>
<td>Atmosphere: Air</td>
</tr>
<tr>
<td></td>
<td>Applied load: 100% of YS</td>
</tr>
<tr>
<td></td>
<td>Test duration (h): 96</td>
</tr>
<tr>
<td>MartInsite®1700 EG</td>
<td>Sample 1</td>
</tr>
<tr>
<td>YS (MPa)</td>
<td>No Cracks</td>
</tr>
<tr>
<td>UTS (MPa)</td>
<td>Sample 2</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>Sample 3</td>
</tr>
<tr>
<td>1600</td>
<td>No cracks</td>
</tr>
<tr>
<td>1720</td>
<td>Sample 4</td>
</tr>
<tr>
<td>3</td>
<td>No cracks</td>
</tr>
</tbody>
</table>

**Table 1. Dimension of the SEP1970 punched hole specimen**
The test typically used by automotive manufacturers or stampers to assess the risk of delayed fracture on hot-stamped parts is the four-point bending test. A rectangular sample can be taken from the part and subjected to a bending stress using an appropriate device. The applied stress can be expressed in percentage of the yield strength (YS) of the material to be tested. This bending test is considered representative of the stress that the part may undergo during clamping for its assembly on the car. On Fig.3, we show the evolution of the stress threshold according to the humidity conditions of the atmosphere in the furnace (dew point) during the austenitization of the blank at 900°C before die quenching. Usibor® 2000-AS can sustain an applied stress much higher than 100% of YS without delayed fracture in a large range of industrial hot-stamping process conditions that can introduce diffusible hydrogen.

**STRESS CORROSION CRACKING: STEP LOAD TEST ACCORDING TO VDA238-201 EXAMPLE ON SEVERAL COATED UHSS (980MPA TO 1700MPA).**

The VDA238-201 [2] describes the step load test (SLT), where a mechanical load is applied in a corrosive solution to simulate exemplary conditions during the vehicle manufacturing process (press shop, body shop, and paint shop) and the life cycle of the vehicles (operating loads and corrosion). In order to be able to compare a wide range of ultra-high-strength steels under similar conditions, we used the most severe specimen (punched hole) subjected to a paint baking treatment (170°C 20min). The specimen is immersed in an aqueous solution containing 5% NaCl at pH7 and is subjected to an incremental mechanical loading described in figure Fig.4. A first stage is applied for 24 hours corresponding to 50% of the breaking load of the specimen Fmax, then the load is increased incrementally by 5% every hour. However, if the material does not survive to the first stage, the level of the first 24-hours is reduced to 25% in order to validate a threshold.
Fig. 5 shows the evolution of the corrosion threshold stress obtained by this incremental maintained loading test as a function of the resistance of the material. The figure clearly shows that this SCC threshold decreases with an increase of the material resistance if we consider only nominal stress. Nevertheless, by using the numerical simulation of the SEP1970 test, it is possible to access to the maximum stress at the edge of the hole for each of the steels considered. In that case and as highlighted by the Fig.5, this local stress remains in the same order of magnitude for these different ultra-high-strength steels.

However, no material acceptance criteria have been clearly defined for the use of this test as well in threshold stress or in percentage of the maximum applied load. It is therefore difficult at this stage to use this test for material approval.

**STRESS CORROSION CRACKING_THRESHOLD USING FOUR-POINT BENDING TEST ON USIBOR®2000-AS IN SEVERAL CORROSION CONDITIONS**

Two main types of accelerated corrosion test have been selected to simulate the introduction of hydrogen during corrosion in the four-point bending test:

- Immersion tests in different corrosion media with often different pH.
- Cyclic corrosion tests which will combine different temperatures but also different humidity phases (dry phase, wet phase), also associating salt spray with rather neutral pH.

**Immersion tests:**

- Immersion tests in HCl pH 1 are not recommended because they strongly amplify the galvanic coupling between the AS coating and steel (no such situation will be encountered in real life) and, therefore, metallic coatings are dissolved in a few hours. This dissolution of coatings leads to intense hydrogen formation and the hydrogen uptake can be then much higher than that linked to atmospheric corrosive conditions.

- Immersion tests in NaCl 5% pH 7 for coated steel are considered as the most relevant to evaluate corrosion risks on cars in service.
Cyclic Corrosion Test (CCT):  
CCT test have been developed for their corrosion representativeness but are they representative of H intake kinetics in real vehicle life situation?

In Table 2, we have selected 3 different accelerated corrosion tests which differ in their duration, their temperature, their salt spray solution (%NaCl, PH) and their alternation of dry and wet phase.

<table>
<thead>
<tr>
<th>Test</th>
<th>Typical duration</th>
<th>Salt Spray phase</th>
<th>Dry phase</th>
<th>Wet phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NaCl</td>
<td>Temperature</td>
<td>Duration (% of cycle time)</td>
</tr>
<tr>
<td>CCT-A</td>
<td>200 cycles (1 cycle = 8 h)</td>
<td>5% NaCl pH 7</td>
<td>35°C</td>
<td>50%</td>
</tr>
<tr>
<td>CCT-B</td>
<td>42 cycles (1 cycle = 1 day)</td>
<td>1% NaCl pH 4</td>
<td>35°C</td>
<td>2%</td>
</tr>
<tr>
<td>CCT-C</td>
<td>6 cycles (1 cycle = 1 week)</td>
<td>1% NaCl pH 7</td>
<td>35°C</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>Temperature from 25°C to 50°C + transitions dry - wet</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Description of Cyclic Corrosion Test CCT1, CCT2, & CCT3

Four-point bending test with different corrosion conditions:  
For Usibor® 2000 AlSi, the results of the four-point bending test indicate that low SCC threshold resistances correspond to the most corrosive tests (Fig. 8). Initially, these tests have been developed to simulate, in a short period of time, the corrosion as it will occur on a car after several years of use. But steel corrosion is the result of both oxygen and water reduction, the last one leading to the formation of hydrogen. Accelerating steel corrosion should then result in hydrogen formation rate much higher than in service conditions. Furthermore, a cyclic test (CCT), being an alternation of several phases (salt spray, dry and humid phases), the SCC risk will be enhanced during the most corrosive phase of the test. In cyclic tests, the maximum steel corrosion rate may be 10 to 30 times higher than in field or on vehicle.

Fig.8. SCC threshold resistance of Usibor 2000-AS is dependent on accelerated corrosion test conditions and therefore on steel corrosion rate.

Table 3. Maximum steel corrosion rate in CCT, field and truck exposure

The criticality of the SCC test will depend on the applied stress, mechanical severity and corrosion aggressivity. As it seems difficult to define what is the most representative compromise, we have chosen to take a laboratory specimen simulating an automotive component, to which all the manufacturing stages of the automotive process will be applied. At last, the component is tested in the most aggressive cyclic corrosion test (VDA233-102, see figure CC)

STRESS CORROSION CRACKING ON A LAB COMPONENT ON TWO UHSS: MARTINSITE® 1700 EG AND USIBOR®2000-AS.

The aim of this section is to assess the delayed fracture risk on a representative component with residual stresses due to forming and welding. This lab component is an over-bent omega shaped rail (to promote residual stresses) closed by a welded plate to get the final shape (Fig.9). In the middle of the component, a wedge is inserted between the central spot welds to simulate the effect of embossments of a real part (gap effect). It is therefore a self-stressed component (over...
industrial conditions) with high residual stresses on the central spot welds. Finite element simulations have been performed to evaluate local stresses and confirmed by X-Ray measurement, cartographies in terms of maximal principal stress are shown in Fig.10 and Fig.11. In the case of the Usibor®2000-AS specimen, welded patches made of zinc-coated materials were added in order to cause galvanic coupling and increase the introduction of hydrogen during the corrosion test. This was not necessary for the MartiNsite1700 EG steel already coated with Zn.

![Fig.9. Self-stressed welded component manufacturing.](image)

![Fig.10. Finite element simulations of the omega shape component](image)

![Fig.11. X-Ray stress measurements](image)

To investigate the impact of corrosion in the most strained areas, six weeks of cycling corrosion tests [3] were performed on lab components whose e-coat in radii and spotwelds were scratched. The results are summarized in the Table 4 for both materials. As illustrated in figures 12 and 13, no stress corrosion cracking was observed on all tested samples made with, respectively, MartINsite® 1700-EG and Usibor® 2000-AS.

<table>
<thead>
<tr>
<th>Tested Material</th>
<th>Sample Type</th>
<th>Corrosion Conditions</th>
<th>Specimen follow-up after 6 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Spot weld</td>
</tr>
<tr>
<td>Usibor® 2000-AS</td>
<td>6 x self stressed omega</td>
<td>VDA233-102</td>
<td>no cracks</td>
</tr>
<tr>
<td>MartINsite® 1700-EG</td>
<td></td>
<td></td>
<td>no cracks</td>
</tr>
</tbody>
</table>

Table 4. Summary of CCT test results on Usibor® 2000-AS and MartINsite® 1700-EG
CONCLUSION

• Delayed fracture tests carried out in air, such as the SEP1970, to validate the risk of the material on delivery condition or the 4pt bending test to validate the conditions of use of a material for hot-stamping are well-defined and have established a material acceptance criterion for material or part approval. MartINsite® 1700 EG and Usibor®2000-AS satisfy those approval criteria.

• Stress corrosion cracking tests, based on similar mechanical tests but in a corrosion medium, permit easily to compare materials with a similar test or corrosion conditions for a given material. For instance, the step load test describes clearly the testing conditions but the minimum acceptable threshold for a safe use of the material in the car is not given. On the other hand, the four-point bending test performed on Usibor® 2000-AS with different corrosion conditions show us that the threshold is directly dependent on the corrosion condition and especially the corrosion rate.

• A method to assess more realistic delayed fracture and stress corrosion cracking risks was proposed. It is based on the testing of lab components which aims to be as most as representative of real parts life (over the industrial constraints). The methodology was applied on 2 UHSS grades: a 1700MPa Martensitic steel and a Press hardened steel of 2000MPa tensile strength which could be considered at an elevated risk level. The e-coated and scratched self-stressed lab components do not exhibit any delayed crack after manufacturing stages and cyclic corrosion tests (VDA 233-102). With respect to body in white applications with similar conditions to this study, no hydrogen cracking should be observed.

REFERENCES

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2. VDA238-201: Testing of the susceptibility of advanced high strength steel sheets to hydrogen induced cracking / Step Load Test