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Investigation of mechanical tests for hydrogen embrittlement in automotive PHS steels

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Received: date; Accepted: date; Published: date

Abstract: the problem of hydrogen embrittlement in Ultra High Strength Steels is well known. Slow Strain Rate, Four Points Bending and permeation tests were performed with the aim of characterizing innovative materials with an ultimate tensile strength higher than 1000 MPa. The hydrogen uptake, in case of automotive components, can take place during manufacturing process: during hot stamping, due to the presence of moisture that at high temperature dissociates giving rise to atomic hydrogen, or also during electrochemical treatments like cataphoresis. Moreover, possible corrosive phenomena could be a source of hydrogen during automobile life.
A test campaign was performed in order to characterize two innovative Press Hardened Steels (PHS), USIBOR 1500 ® and USIBOR 2000 ®, and to establish a correlation between ultimate mechanical properties and critical hydrogen concentration.

Keywords: Hydrogen Embrittlement, Ultra High Strength Steels, Automotive, Press Hardening Steels, Hydrogen Induced Delayed Fracture, Diffusible Hydrogen

1. Introduction

The priority of maintaining and, if possible, increasing the safety of drivers and passengers collides with the necessity of reducing the CO_2 emissions and so the weight of vehicles. In this contest the research and characterization of new materials with the possibility of emissions reduction are more and more diffused. To reduce thicknesses of sheets, higher tensile properties are required and a major hydrogen susceptibility is the natural consequence.
Advanced high strength steels (AHSS) exhibit considerable mechanical properties and a good formability and during the production process hydrogen could be adsorbed in various phases: pickling, electroplating, cataphoresis and phosphating or even moisture during welding or heat treatment, can cause an introduction of hydrogen in the material.
Press Hardened Steels (PHS) are hot formed steels and used in automobile structural and safety components and present high homogeneity of mechanical properties and excellent fatigue resistance: their manufacturing process consists mainly of an austenitizing of blanks in a oven and following martensitic quenching in the water-cooled stamping tool.
The main source of hydrogen for this kind of materials is the hot stamping process: hydrogen comes from the dissociation of water at high temperature, adsorption and absorption in the steel bulk and its entrapment after water-cooling quenching.
The hydrogen present in the material can diffuse and concentrate in microstructural vacancies or defects and crack the material giving rise to the so called Internal Hydrogen Embrittlement (IHE), related to hydrogen charging before service.
The most known mechanisms that try to explain the interaction and behavior of hydrogen [1] with steel are HEDE (Hydrogen Enhanced DEcohesion) and HELP (Hydrogen Enhanced Local Plasticity):

the first one assumes that hydrogen gives a contribution to the tensile strength: the higher the hydrogen concentration higher the hydrogen pressure and decohesion of steel atoms; the latter suggests that hydrogen, moving towards crack tips where hydrostatic stress is higher, promotes dislocations motion and reduces the interaction energy of them with internal obstacles with consequent formation of micro-voids.
Two different conditions were studied and compared in this work: on one side the Slow Strain Rate Tests, so a very slow imposed deformation of the material, in order to give hydrogen necessary time to hydrogen to concentrate in the plastic zone; on the other hand there was the study of static behavior of materials investigated by means of Four Point Bending Tests.
In addition, a permeation test campaign was performed to evaluate the diffusion coefficient and its dependence on thermal treatment.
The aim of this activity was to determine a practical and easy-applicable methodology to study the susceptiblity to hydrogen of Ultra High Strength Steels for automotive industry.

2. Materials and Methods

2.1. Materials

The material under investigation [2] is a patented ultra-high strength Aluminum-Silicon coated boron steel. Two grades were studied, one with 1500 MPa of UTS and one with 2000 MPa.
These materials are subjected to hot forming process and they are used in structural and safety automobile components.
After the thermal treatment the microstructure is completely martensite and thus susceptibility to hydrogen embrittlement increases.

Table 1 Chemical compositions of the two steels (wt %)

	C	Si	Mn	P	S	Al	B	Ti	Cr
USIBOR 1500 ®	0,19	0,21	1,13	0,015	0,008	0,0038	0,003	0,031	0,19
USIBOR 2000 ®	0,38	0,19	1,21	0,013	0,006	0,032	0,0032	0,024	0,28

Mechanical properties of the two materials are shown in Table 2:

Table 2 Mechanical properties of materials under investigation

	$R_{P,02}$ [MPa]	R_m [MPa]	A_{50} [%]
1500 Grade	1252	1485	7,3
2000 Grade	1510	1881	6,2

The difference in mechanical properties has to be imputed to a major content of C in USIBOR 2000 ®.

2.2. Hydrogen Charging

A charging by electrochemical way was achieved, immerging the samples in a solution and imposing a current between cathode (the sample) and anode (platinum mesh) simulating the cataphoresis process. Used solutions containing NaCl and NH_4SCN [3], the variation and combination of current and solution's composition, in particular in terms of recombination's poison, allowed to vary the hydrogen concentration absorbed by the material.
In this work NH_4SCN varied in the range of 0,03-0,3 % and current in the range of 0,25-1 mA/cm^2 to avoid surface damage.
Every sample was further treated by introducing it in the laboratory furnace and heating material at the temperature of 150 °C for 10 minutes simulating paint baking industrial process: in this way a

uniform hydrogen distribution was achieved inside the material and, according to [4], not a considerable amount of hydrogen was desorbed.
In Figure 1 the electrochemical device for hydrogen charging is depicted:

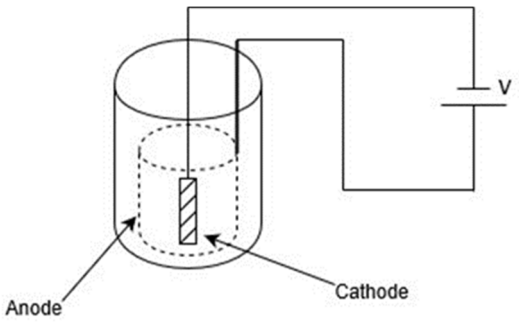


Figure 1 Electrochemical cell for hydrogen charging

2.3. Slow Strain Rate Tests

The slow strain rate tests were performed referring to ASTM G129 [5] setting a crossbar velocity of 0,001 mm/s; the very slow rate corresponds to a very low deformation rate: in this way hydrogen is able to migrate towards the following fracture zone.
The geometrical and dimensional characteristics according to[6] of the sample used in these tests are shown in Figure 2:

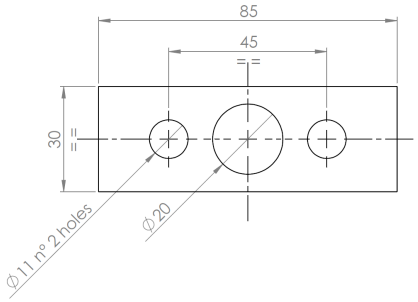
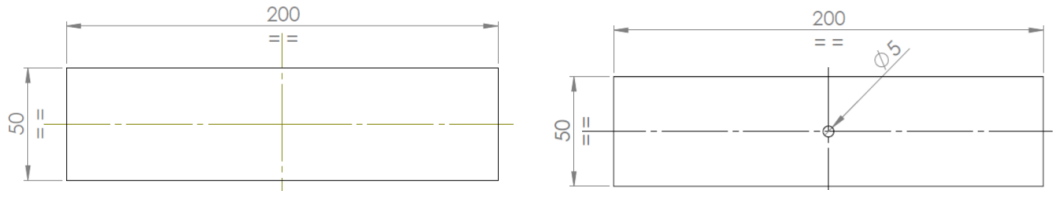


Figure 2 SSRT sample

2.4. Four Point Bending Tests

The experimental method provided four point bending (4PB) tests to evaluate the susceptibility of the steel to delayed fracture due to hydrogen; 4PB tests were carried out referring to ASTM F-1624 [7]; the dimensions of samples used in those tests are represented in
Figure *3*.



(a) (b)

Figure 3: Dimensions and geometry of (a) four point bending test samples without hole and (b) with

The loading consists of increasing the stress to which the material is subjected progressively, always in the elastic range, starting from 50% of $R_{p,02}$; this load was maintained for 24 h, then it was increased every 2 hours up to 90%.

It must be noticed that in case of rupture the hydrogen content was immediately evaluated by hot extraction method to correlate the concentration of hydrogen to the critical load.

Once reached the 90% of $R_{p,02}$, the final test was to keep the sample in this condition for other 24 hours. If the sample didn't fail it was declared *safe*.

In Figure 4 is shown the device to carry out the four point bending tests.

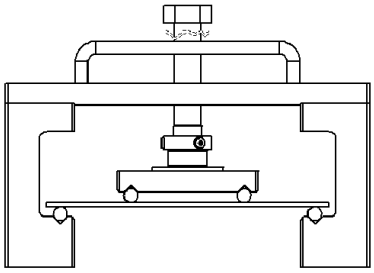


Figure 4 Four point bending tests equipment

2.5. Permeation Tests

Permeation tests referred to ISO 17081:2004 [8] were carried out with the aim of characterizing material in terms of diffusion coefficient and by means of an innovative instrument patented by Letomec S.r.l that uses a solid state hydrogen-sensitive sensor [9]: sample was located between an electrochemical cell and the probe of the instrument and a current between cathode (sample) and anode (a platinized titanium mesh) was applied, as the discharge of hydrogen occurred in the surface in contact with solution of 3% NaCl and 0,3% NH_4SCN and current density was 0,5 mA/cm^2, then hydrogen was adsorbed and diffused through the specimen thickness, reaching the outside surface where the solid state sensor detected it. In Figure 5 appears the scheme of the instrument.

The reaction of hydrogen discharge takes part in the sample's surface M in contact with the solution:

$$\boldsymbol{H_2O + M + e^- \rightarrow MH_{ads} + OH^-} \quad (\mathbf{1})$$

In this way, according to Volmer's theory [10], the atom of hydrogen could be adsorbed by the material and, in a second moment, be absorbed in the bulk or recombine to give molecular hydrogen (moving away in the form of gas bubbles).

The absorbed hydrogen reaches the outside surface where the sensor's probe is applied, leaves the sample and passes through the probe and is detected: as a result, the typical permeation curve is obtained.

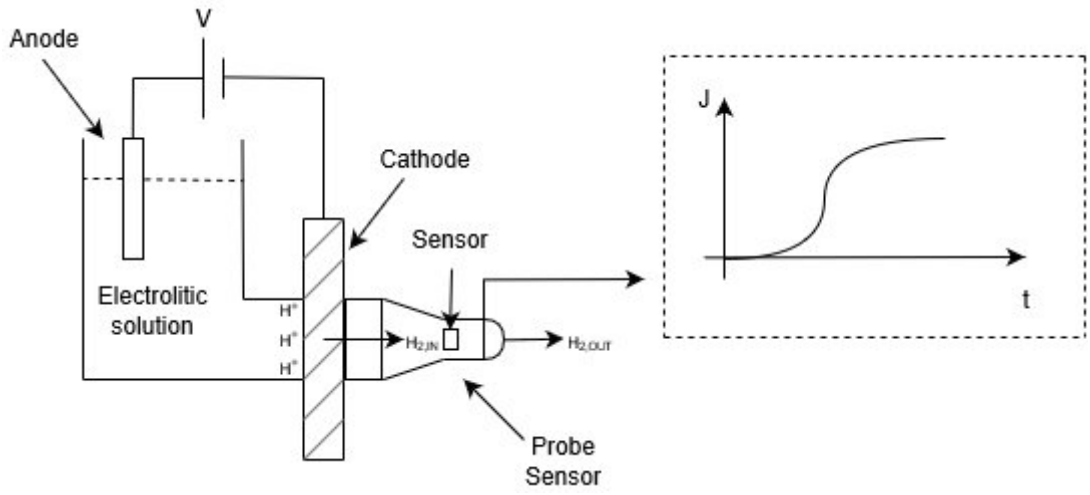


Figure 5 Innovative instrument patented by Letomec S.r.l

2.5. Hydrogen Measurement

For 4PB and SSR tests the concentration of hydrogen was evaluated by hot extraction method by means of *Leco* DH603 instrument: samples were heated at 265 °C in order to guarantee the complete desorption of diffusible hydrogen.

3. Results

3.1. Slow Strain Rate Tests

The Slow Strain Rate tests were carried out on hydrogen pre-charged samples : after the sample fracture the content of hydrogen was measured, details in the previous paragraphs.

In Figure 6 and Figure 7 were reported the two characteristics of the two different materials.

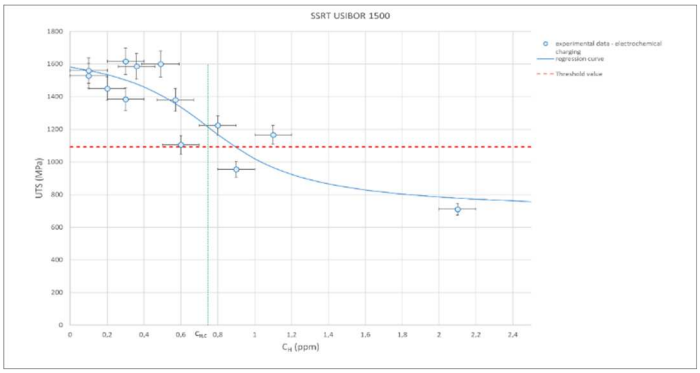


Figure 6 SSRT for USIBOR 1500 ®

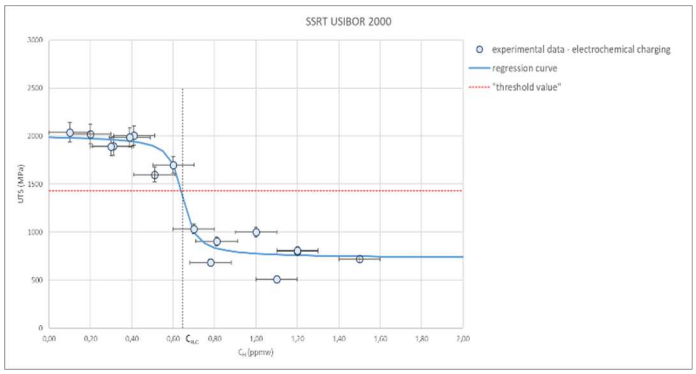


Figure 7 SSRT for USIBOR 2000 ®

In the figures above, $C_{H,C}$ represents the critical concentration obtained by the inflection point of the regression curve, correspondent to parameter m_3.The error bars depend on the sensitivity of *Leco* DH603, equal to $\pm$ 0,1 ppmw while on the y-axis the error value is 5 %, derived from uncertainty on the measure of the sample's thickness.

3.2. Four Point Bending Tests

In Figure 8 are shown the 4PB test results for USIBOR 1500 ® while in Figure 9 those related to USIBOR 2000 ®; the $C_{H,C}$ is again the critical concentration found as the inflection point (and equal to m_3 in the regression equation); as for the SSR tests the materials presented a first asymptote for low concentrations, a dramatic fall for a critical concentration and a second asymptote meaning a saturation effect [11]

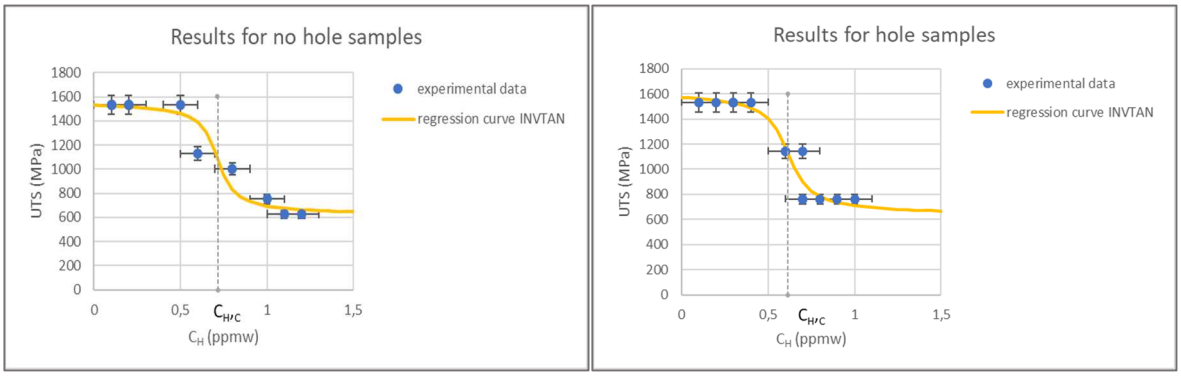


Figure 8 (a) No hole samples (b) Hole samples USIBOR 1500 ®

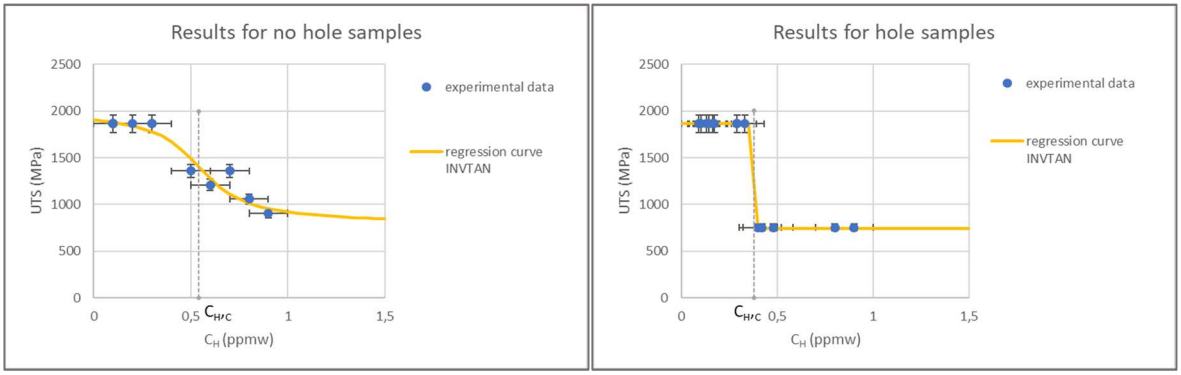


Figure 9 (a) No hole samples (b) Hole samples USIBOR 2000 ®

3.3. Permeation Tests

Sample thickness was equal to 1,4 mm in this particular case for both materials, the two steels were both undergone to permeation tests before and after hot stamping treatment to study the effect of microstructure transformation. In Figure 10 are compared the results:

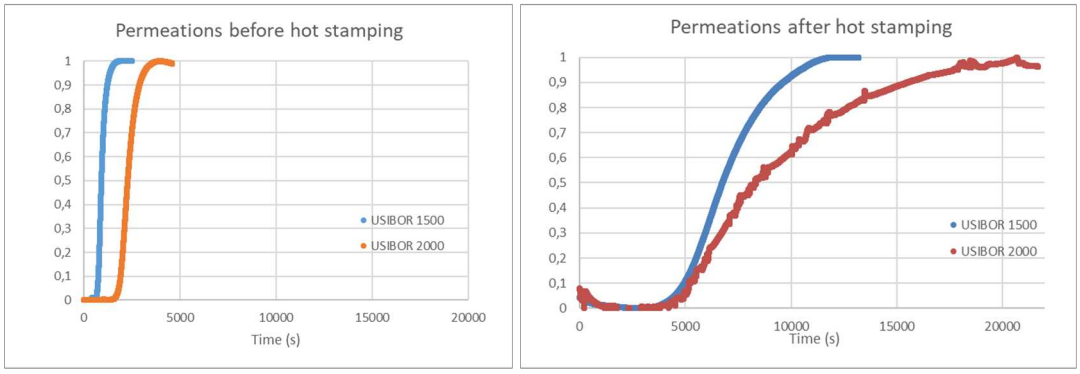


Figure 10:(a) Permeations cure before hot stamping (b) Permeations curve after hot stamping

As said before, in Table 3 are shown the diffusion coefficients for the two different materials under investigation: according to international literature [12], the differences underlined before are evident.

Table 3 Diffusion coefficient for the two grades steels as a function of thermal treatment

	Diffusion coefficient (m^2/s)	
	Before Hot Stamping	**After Hot Stamping**
1500 Grade	3,39E-10	4,50E-11
2000 Grade	1,36E-10	3,25E-11

3.3. SEM Images

In Figure 11 SEM images are shown and typical intergranular fracture surface is illustrated:

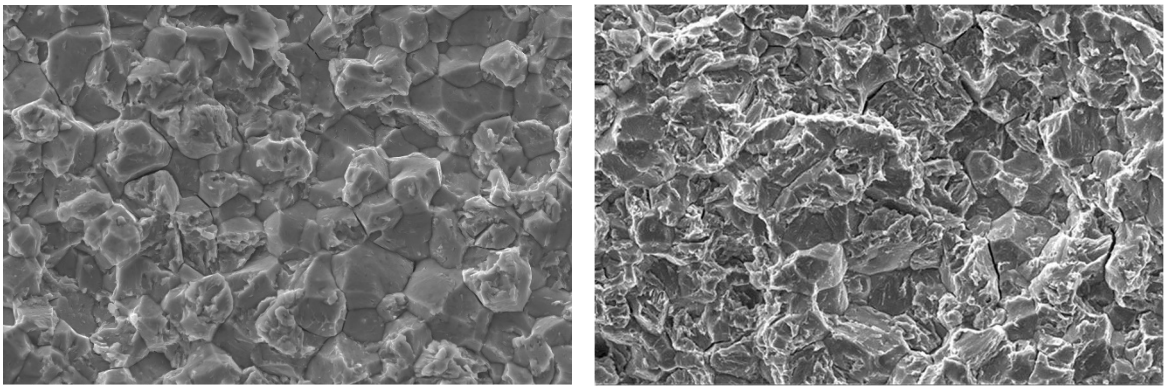


Figure 11 (a) USIBOR 1500 ® (b) USIBOR 2000 ®

For both pictures the magnification is 5000x and the hydrogen content, absorbed by the samples, was 2,1 ppmw and 0,5 ppmw, respectively.

3.4. FEM Simulation

The FE model was simplified representing a quarter of the sample considering symmetry planes. Loading cylinders and sample were linked together with contact elements, which allowed the contact region to move in function of the deformed shape, taking into account the non-linearity of geometry (big displacements). For holed specimens FEM simulation returned a stress concentration factor value close to 2.

In Figure 12 is shown the quarter of sample and with a red dot is highlighted the node correspondent to the maximum of hydrostatic stress.

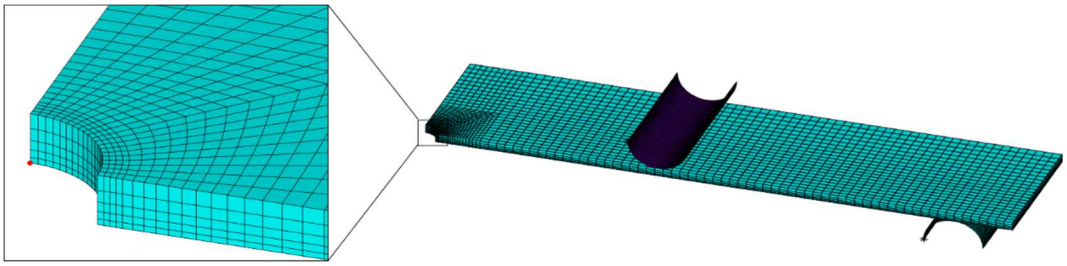


Figure 12 FEM images representing point of maximum hydrostatic load (red dot)

4. Discussion

4.1. Hydrogen diffusion and degradation

The diffusion phenomenon is regulated by the Fick's laws and even the movement of hydrogen atoms inside a steel can be described by means of Fick's equations. Experimental tests demonstrated a behaviour a little far from the ideal theory: this difference is due to the presence of hydrogen traps inside the metals lattice such as dislocations, grain boundaries, precipitates and so on.

Traps influence the diffusion of atoms in the bulk and they are divided in two categories: reversible and irreversible, depending on their own binding energy related to the traps (irreversible are those traps that release hydrogen at a temperature higher than 1000 °C while, according to literature, the reversible hydrogen leaves steel at a lower temperature, in particular for USIBOR it is equal to 265 °C [13]).

According to McNabb et al. (1963) model [14], traps saturate and the equations that rule this phenomenon are shown below [12]:

$$\begin{cases} \dfrac{\partial C}{\partial t} = D\dfrac{\partial^2 C}{\partial x^2} - N_r\dfrac{\partial v}{\partial t} - N_i\dfrac{\partial w}{\partial t} \\ \dfrac{\partial v}{\partial t} = K_r C(1-v) - pv \\ \dfrac{\partial w}{\partial t} = K_i C(1-w) \end{cases} \quad (2)$$

Where C is the hydrogen concentration (atoms/m^3), D the hydrogen diffusion coefficient (m^2/s) in pure iron, N_r and N_i are the concentration of reversible and irreversible traps respectively (atoms/m^3), v represents the occupied reversible traps fraction while w refers to irreversible traps, t and x the time and space variables; K_r is the trapping rate for reversible traps (m^3/atoms s), K_i is the same for irreversible traps and p is the release rate for reversible traps.

As it can be noticed in table 4 and according to [12], traps are dislocations generated from the phase transformation during the quenching process and the diffusion is always faster in USIBOR 1500 ®

than USIBOR 2000 ® for the major quantity of carbon in the second one; moreover the thermal treatment reduces the diffusion coefficient of hydrogen.

The embrittling process [15] is related to the interaction of atomic hydrogen with interatomic bonds and when the cohesive strength of the material is overcome, the crack propagation occurs, referring to the I mode of crack growth according to mechanical fracture. At the crack tip, the presence of a high pressure gradient increases the solubility of hydrogen in the lattice due to lattice expansion, resulting in a hydrogen flux towards this region.
According to HEDE model the cohesive strength is affected only by lattice hydrogen C_L and its dependence is shown in the following equation:

$$\sigma_N^c(C_L) = \sigma_N^c(1 - a_1\theta_s + a_2\theta_s^2) \quad (3)$$

With a_1 and a_2 empiral constants and θ_s defined as:

$$\theta_s = \frac{C_L}{C_L + \exp\left(-\frac{\Delta H}{RT}\right)} \quad (4)$$

Where ΔH is equal to 30 kJ/mol, R the gas constant and T absolute temperature.
The hydrogen concentration tends to accumulate next to the crack tip because of higher hydrostatic stresses, according to the well known Beck's law [16]:

$$C = C_L \exp\left(\frac{V_H \sigma_H}{RT}\right) \quad (5)$$

Where V_H is the molar volume of hydrogen in the lattice, equal to 2E-06 m^3/mol, σ_H is the hydrostatic tension, R the gas constant, T the absolute temperature, C_L the concentration of hydrogen without stress and C the concentration near the crack tip in presence of stress [17].
The accumulation of hydrogen in potential cracking initiation sites depends on the strain-stress time gradient and diffusion coefficients [18]:

$$\frac{\partial C}{\partial t} = D\nabla^2 C + D\frac{V_H}{R(T - T^z)}\nabla C\nabla p + D\frac{V_H}{R(T - T^z)}C\nabla^2 p \quad (6)$$

Where C is the hydrogen concentration, D the diffusion coefficient, T^z the absolute zero temperature, p the hydrostatic stress.
In international literature it is possible to find various studies of numerical and theorical simulation in order to explain the hydrogen embrittlement phenomena [18**].**
In automotive industry very thin thickness (0,5-2E-03 m) sheets are used and for this reason a more practical approach is reasonable.
The extrapolation of a regression curve, figure 6 and figure 7, able to describe the behavior of the steel[19,20] and the correspondent equation were derived:

$$UTS\ (MPa) = m_1 - m_2 \cdot arctg\left(\frac{C_H - m_3}{m_4}\right) \quad (7)$$

From the function's study the point where the second derivative is equal to zero has abscissa equal to $C_H = m_3$ and this is very close to the value of critical hydrogen concentration, obtained according to [21], for both steels.

The same was done for the Four Point Bending Tests and from the mathematical expressions, critical hydrogen concentration was found for both materials, summarized in Table 4:

Table 4 Critical Hydrogen Concentration for the different mechanical tests

	USIBOR 1500®	**USIBOR 2000®**

4PB Hole	0,61	0,37
4PB No Hole	0,71	0,54
SSRT	0,74	0,64

The worst conditions are given by the presence of hole in 4PB samples; differently from the SSR specimens where the deformation rate is higher than the diffusion and the hole creates an intensity factor really near to 1: for this reason, the accumulation of hydrogen in the SSR sample is negligible while a more emphatic effect can be noted in the 4PB with hole. The 4PB without hole samples showed a concentration closer to SSRT specimens, even though the difference in test time duration, due to the absence of stress gradient.
In Figure 13 is represented the evolution of hydrogen concentration at the crack tip as a function of test time.

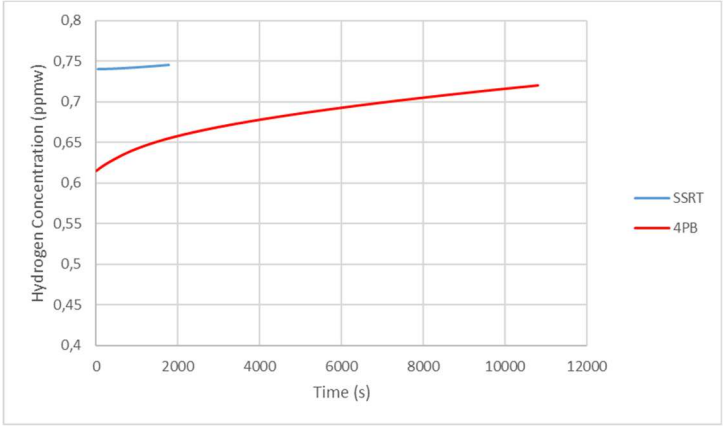


Figure 13 Hydrogen accumulation at the crack tip during the test. Note: simulation is related to USIBOR 1500®

5. Conclusions

From the different mechanical tests on USIBOR 1500 ®and USIBOR 2000 ®, the following conclusions can be summarized:

- These steels are sensitive to the hydrogen delayed fracture and the grade 2000 is quite more sensitive than grade 1500.
- The 4PB tests with hole are the most severe because the failure occurs with a minimum average concentration.
- The hydrogen diffusion strongly decreases after hot stamping and quenching process because of the martensite formation; moreover, because of the higher amount of carbon, grade 2000 has a slower diffusion.
- The differences in critical hydrogen concentration values for the mechanical tests is due to two factors:
    1. The effect of deformation rate in the SSRT that gives a minor time to hydrogen to diffuse near the crack tip.
    2. The presence of the hole in the 4PB samples induces tension gradients that, coupled to time, create hydrogen accumulation near the crack tip.
- Finally, the 4PB with hole is absolutely the most realistic test to simulate the risk of hydrogen embrittlement for this type of materials; however the SSR test can represent a quick method to compare different materials behavior in presence of hydrogen.

Author Contributions: S.C., R. V. and M.V. designed and conceived the experiments; M.V., S.C. and L.B. performed the experiments; all the authors analyzed data; M.M.T. provided materials; M.V. and R.V. wrote the paper.

Acknowledgments: Authors desire to thank Eng. Barile and Eng. Thierry (Arcelor Mittal) for materials; Prof. Bernardo Monelli and PhD student Francesco Aiello for FEM simulation.

Conflicts of Interest: The authors declare no conflict of interest.

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