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Design of a non-destructive test for validating models of hydrogen migration

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Abstract. High-strength steels, despite their excellent mechanical properties in normal conditions, can be susceptible to hydrogen embrittlement. Due to the service loads or residual stresses, hydrogen migrates within the component and accumulates in the regions where the highest tensile hydrostatic stress occurs. As a consequence, component brittle failure can occur even if the initial or mean hydrogen concentration is lower than the critical value. The availability of models predicting the hydrogen diffusion within the component is a crucial task for the design. Several diffusive models have been presented in the literature and some general-purpose finite element codes have already implemented some of them. However, the validation of those models is still an open issue due to the difficulty in performing accurate local measurements of the hydrogen concentration. This study deals with the design of a test potentially able to validate hydrogen migration models. In the test, a four-point bending configuration is applied to a properly shaped hourglass specimen, previously charged with hydrogen, extracted from thin high-strength steel sheets. The specimen geometry and the loading configuration were designed to obtain a central region in which the stress and strain field is uniform in plane and exhibits a quasi-uniform gradient in the thickness direction. As a consequence, it is expected a large enough central region of the specimen in which the Hydrogen can migrate only in the thickness direction during the typical duration of the test. The local hydrogen concentration is evaluated by measuring the flux leaving the tensile surface of the specimen by a solid-state hydrogen sensor.

1. Introduction

Hydrogen can be present in mechanical components as a consequence of production, assembling and finishing processes of a component or from exposure to the service environment. When the hydrogen concentration reaches a critical value a strong reduction of mechanical properties, particularly ductility, toughness, and strength, is observed and also metals with a significant ductility can behave in a very brittle way, [1,2].

Hydrogen concentration gradients and hydrostatic stress gradients are known to be the drivers of the hydrogen migration in steel components. Due to the hydrostatic stress gradients, caused by operating loads applied on the component or residual stresses, the diffusible hydrogen, already present in a component, tends to migrate towards the regions with the highest tensile hydrostatic stress, where the lattice expanded by the stress provides more favorable sites for the small hydrogen atoms, [3–5]. As a consequence, the hydrogen-induced embrittlement affects mainly the regions already critical for the risk of brittle failure. In order to assess the component strength in operating conditions, either under static or time-varying loads, it is worth developing a model that can predict the hydrogen distribution.

Lattice defects, such as vacancies, precipitates, grain boundaries and dislocations, consequences of plastic strains, provide energetically favored sites (called "traps") for hydrogen atoms and can significantly affect the hydrogen diffusion and distribution, [6,7]. The potential energy of a hydrogen atom close to a lattice defect, produced during thermal or mechanical processing, is lower than that in regular interstitial lattice sites, due to the electronic interactions with atoms in an elastically strained lattice. The traps are usually divided into reversible and irreversible ones, on the basis of the energy required to the hydrogen atom for leaving the site. If the trapping energy is high, the hydrogen atoms cannot leave the site at the component operating temperature and the trap is considered "irreversible". The hydrogen atoms trapped in the irreversible traps do not contribute to the diffusible hydrogen, [8].

Several models have been proposed in the literature for describing the hydrogen diffusion in metals, and several general-purpose finite element codes have already implemented some of them. However, the validation of these models is still an open issue because of the difficulty in performing the local measurement of the hydrogen concentration.

A controllable and uniform hydrostatic stress gradient, aimed at producing a uniform hydrogen concentration in an area where hydrogen concentration can be measured, along with a hydrogen concentration sensor not requiring a destructive test and able to perform a local and in real-time measurement are the requirements for a test configuration suitable for validating a hydrogen migration model.

In the present paper, the design of an experimental test for the validation of stress-driven hydrogen migration models is proposed. The test is based on a constant load bending test on sheet hourglass samples, uniformly hydrogenated before the load application, and on a local non-destructive measurement of the hydrogen concentration. The sample geometry and the loading configuration were devised to obtain a quasi-uniform stress gradient in the sample thickness direction and a quasi-uniform stress field in the hydrogen measurement area. With this configuration, a quasi-uniform final hydrogen concentration on a large enough surface of the sample is produced, thus making it possible to produce a steady and reliable measurement of the hydrogen concentration. A Finite Element Model (FEM), developed to model all the principal phenomena affecting the hydrogen migration in stressed components was used to simulate the test.

2. Methods

2.1. Theoretical formulation

By considering an ideal homogeneous material, where the distribution of hydrogen possible sites in the lattice is uniform, and a component without external loads and residual stresses, the distribution of hydrogen can be derived from the solution of Fick's laws of diffusion:

$$\vec{J} = -\boldsymbol{D}\,\overrightarrow{\nabla C} + \vec{v} \cdot C \tag{1}$$

$$\frac{\partial C}{\partial t} = -div\left(\vec{J}\right) + G \tag{2}$$

where $\vec{J}$ is the diffusion flux density, $\boldsymbol{D}$ the diffusivity tensor, C the atomic concentration, $\vec{v}$ the transport velocity vector and G the diffusing substance generation rate per unit volume.

The presence of microstructural defects (such as dislocations, vacancies, grain boundaries, and precipitates) creates trapping sites, which provide an energetically favored environment for occupancy by the hydrogen, [6].

The Fick's first law is still valid for the hydrogen that occupies normal sites, namely the so-called "diffusible hydrogen", [6]. Writing the equations for a mono-dimensional condition, a typical configuration in the permeation tests used for evaluating the diffusion properties of the material, equation (1) can be simplified as it follows:

$$J = -D_L \cdot \frac{dC_L}{dx} \tag{3}$$

where C_L is the "diffusible" hydrogen concentration and D_L is the normal diffusivity, that it would be obtained in an ideal homogeneous lattice.

The hydrogen transport process is affected by the hydrostatic stress gradient $\nabla \sigma_H$, [3–5]. The first Fick's law, equation (1), has to be modified to include the stress contribution:

$$\vec{J} = -\boldsymbol{D}\,\overrightarrow{\nabla C_L} + \boldsymbol{D}\,\overrightarrow{\nabla \sigma_H} \cdot \frac{C_L \cdot \Omega}{R \cdot T} \tag{4}$$

where $\vec{J}$ is the diffusion flux density, expressed in $\mathrm{mol}/(\mathrm{m}^2 \cdot \mathrm{s})$, $\boldsymbol{D}$ the diffusivity matrix, whose coefficients are expressed in m^2/s, C in the atomic concentration, expressed in $\mathrm{mol/m}^3$, Ω is the molar volume, expressed in $\mathrm{m}^3/\mathrm{mol}$, T is the absolute temperature, expressed in Kelvin, R is the universal gas constant, and σ_H is the hydrostatic stress, expressed in Pa.

The total hydrogen concentration can be expressed as the sum of the diffusible, C_L, and the trapped part C_T [6]:

$$C = C_L + C_T = \theta_L \cdot N_L + \theta_T \cdot N_T \tag{5}$$

where N_T is the trap site density, N_L the interstitial site one, whiles θ_T and θ_L are their occupancy, that is $C_L = \theta_L \cdot N_L$ and $C_T = \theta_T \cdot N_T$.

The relation between the flux observed in experiments, such as in permeation tests, and the gradient of the total hydrogen concentration C can be expressed as [6]:

$$J = -D_{eff} \cdot \frac{dC}{dx} \tag{6}$$

The relation between the "effective", D_{eff}, and the normal D_L, diffusivities, can be derived by assuming that the trapped population is in equilibrium with the population upon normal lattice sites not only in the static (namely, with null flux) situation but also during diffusion, [6]. This assumption is considered accurate enough for steels of industrial interest, [3]. The effective diffusivity D_{eff}, depends on: the microstructure of the material, the traps and the interstitial sites densities and the energy of the traps, ΔE_T, [9]. Aa a consequence, D_{eff} depends on the material and the amount of plastic strain accumulated in the component before the diffusive process. The following relationship is usually adopted for estimating the effective diffusivity:

$$D_{eff} = D_L \frac{1}{1 + \dfrac{N_T}{N_L} \cdot e^{\left(-\frac{\Delta E_T}{RT}\right)}} \tag{7}$$

with D_{eff} to use in place of the normal diffusivity in the Fick's laws (1) and (2), [6,10,11] in order to approximately account for the trapping phenomena.

The transport equation, namely Fick's second law (2), yields to:

$$\frac{\partial C}{\partial t} = \frac{\partial C_L}{\partial t} + \frac{\partial C_T}{\partial t} = -div\left(-\boldsymbol{D}\,\overrightarrow{\nabla C_L} + \boldsymbol{D}\,\overrightarrow{\nabla \sigma_H} \cdot \frac{C_L \cdot \Omega}{R \cdot T}\right) \tag{8}$$

In the case of uniform, but still direction-dependent, diffusivity coefficients, it can be written as:

$$\frac{\partial C}{\partial t} = D_{xx}\frac{\partial^2 C}{\partial x^2} + D_{yy}\frac{\partial^2 C}{\partial y^2} + D_{zz}\frac{\partial^2 C}{\partial z^2} - \frac{\Omega}{R \cdot T} \cdot div\left(\boldsymbol{D}\,\overrightarrow{\nabla \sigma_H} \cdot C\right) \tag{9}$$

where:

$$div\left(\boldsymbol{D}\,\overrightarrow{\nabla\sigma_H}\cdot C\right) = D_{xx}\left(\frac{\partial C}{\partial x}\cdot\frac{\partial \sigma_H}{\partial x} + C\frac{\partial^2 \sigma_H}{\partial x^2}\right) + D_{yy}\left(\frac{\partial C}{\partial y}\cdot\frac{\partial \sigma_H}{\partial y} + C\frac{\partial^2 \sigma_H}{\partial y^2}\right)$$
$$+ D_{zz}\left(\frac{\partial C}{\partial z}\cdot\frac{\partial \sigma_H}{\partial z} + C\frac{\partial^2 \sigma_H}{\partial z^2}\right) \tag{10}$$

2.2. Test configuration for the model validation

Among the standard tests proposed in the literature, the incremental step loading, [12] could be considered suitable for observing the stress-induced hydrogen migration phenomenon. However, these tests are carried out by employing a notched specimen, featuring a v-notch or a hole, that localizes the onset of the hydrogen-induced crack. In those tests, the stress concentration and the consequent hydrostatic stress gradient cause a high hydrogen accumulation in the small region that experiences the highest tensile stresses due to the notch severity.

By adopting the standard methods, such as the Hot Extraction Method (HEM), it is possible to measure only the mean hydrogen concentration in the region near the failure. Moreover, for applying the HEM, it is necessary to remove a part from the specimen after the test, with the risk of reducing the hydrogen content due to the local heat introduced by the cutting processes.

The proposed test configuration overcomes the shortcomings of the previous test and can be suitable for an effective validation of the hydrogen migration models. The model validation will be carried out by measuring the local hydrogen concentration in the proximity of a uniformly stressed surface of the specimen and by comparing measured values with those calculated by the model.

A hydrostatic stress gradient can be generated by a four-point bending loading configuration that produces linearly variable stress in the direction of the specimen thickness and constant bending moment within the two intermediate supports. It was employed an un-notched specimen that, in the central part, features a wide area subjected to an almost in-plane uniform stress field, Figure 1. The blunt width reduction was introduced to have high enough maximum bending stress with not excessive specimen deflection and applied load.

The hydrogen concentration was measured by the Helios 4 Hot Probe (Letomec S.r.l., Pisa, Italy). This device, aimed at producing a local not destructive hydrogen measurement, is based on a solid-state sensor that measures the hydrogen flux desorbed by a controlled region on the specimen surface. In the adopted configuration, the measurement region has a circular shape, with a diameter of about 25mm. The electrical signal produced by the sensor is elaborated and, by means of proper calibration parameters, provides the local diffusible hydrogen content in the sheet metal with a resolution of 0.1 ppmw [13]. The instrument can be used also on surfaces that, at room temperature, are considered almost impermeable to the hydrogen flux, namely surfaces featuring a coating. To this purpose, the probe is equipped with a device that locally heats the component to increase the diffusivity of the coating, allowing the hydrogen to pass through the coating.

The sensor was applied in the central region of the specimen, dashed area in Figure 2, which features a high hydrostatic stress gradient, in the direction of the specimen thickness, and an almost uniform stress in the directions normal to the thickness. The hydrogen concentration and the desorbed flux can be considered uniform in the area exposed to the sensor. The test configuration allows for either a continuous or an intermittent measurement during the test as the Helios IV device can be applied on the tensile side of the specimen which is accessible also under the bending test, as shown in Figure 3.
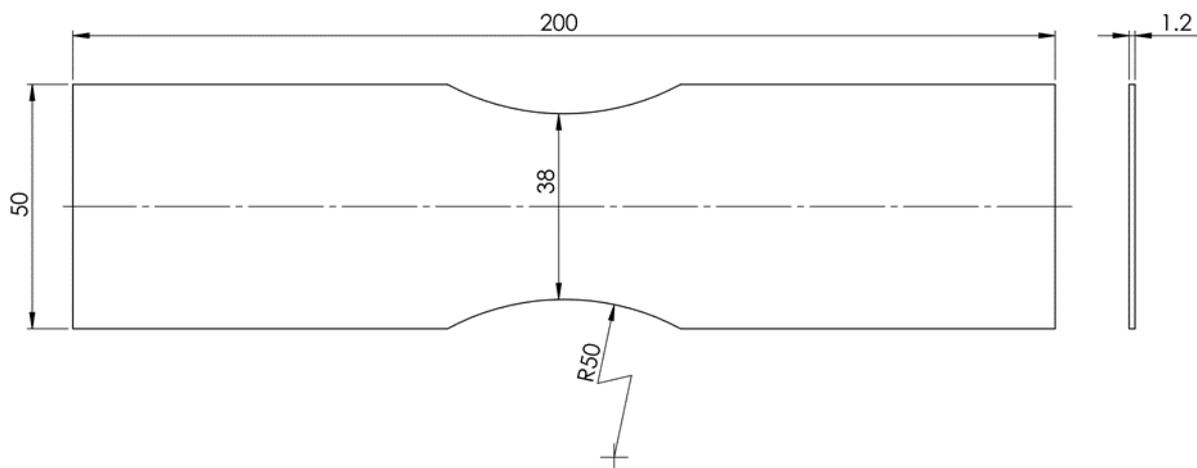
**Figure 1.** Drawing of the specimen.
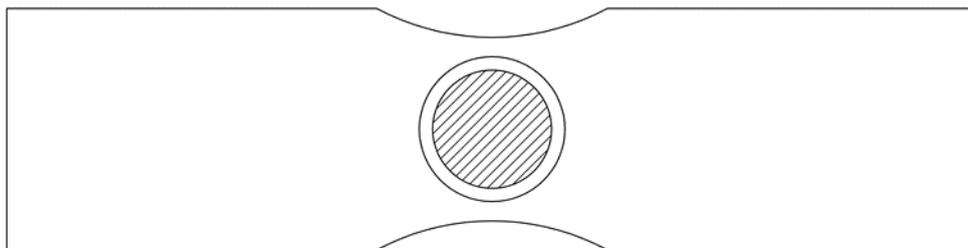
Figure 2. Desorbed region of the specimen (dashed area).

The load was applied in displacement control, by using a calibrated bolt to set the specimen's deflection, Figure 3. The specimen deflection is directly measured by using a caliper before starting the test, with a resolution that is equivalent to a variation of 1% in the maximum stress occurring in the specimen. It was applied a load that produced only elastic strains, with the maximum in-plane stress component equal to the 50% of the material yield strength (S_y).

Hydrogen charging was applied to the stress-free specimen by an electrochemical device. Three nominally identical samples are immersed in a conductive water solution and a controlled constant electric current between the cathode (the samples) and the anode (a platinum mesh) was imposed. When an electrical potential is applied across the electrodes, the electrolytic solution decomposes and hydrogen ions (protons) are produced on the specimen surface, [14]. Electrochemical charging time was calculated on the basis of the formulation presented by Crank, [15], and depends on the specimen thickness, the presence of surface coatings, and the hydrogen diffusion coefficient at the charging temperature, obtained from permeation tests. The room temperature during the charging process is continuously monitored by a digital thermometer having a resolution of 2°C.

To induce a uniform initial hydrogen distribution in the specimen, after the electrochemical charging, the specimens were kept in a furnace at a temperature lower than the value that produces significant hydrogen desorption. The hydrogen content was then measured either by HEM or by the Helios IV probe on one of the specimens, while the other two, with the same hydrogen content, are mechanically tested.
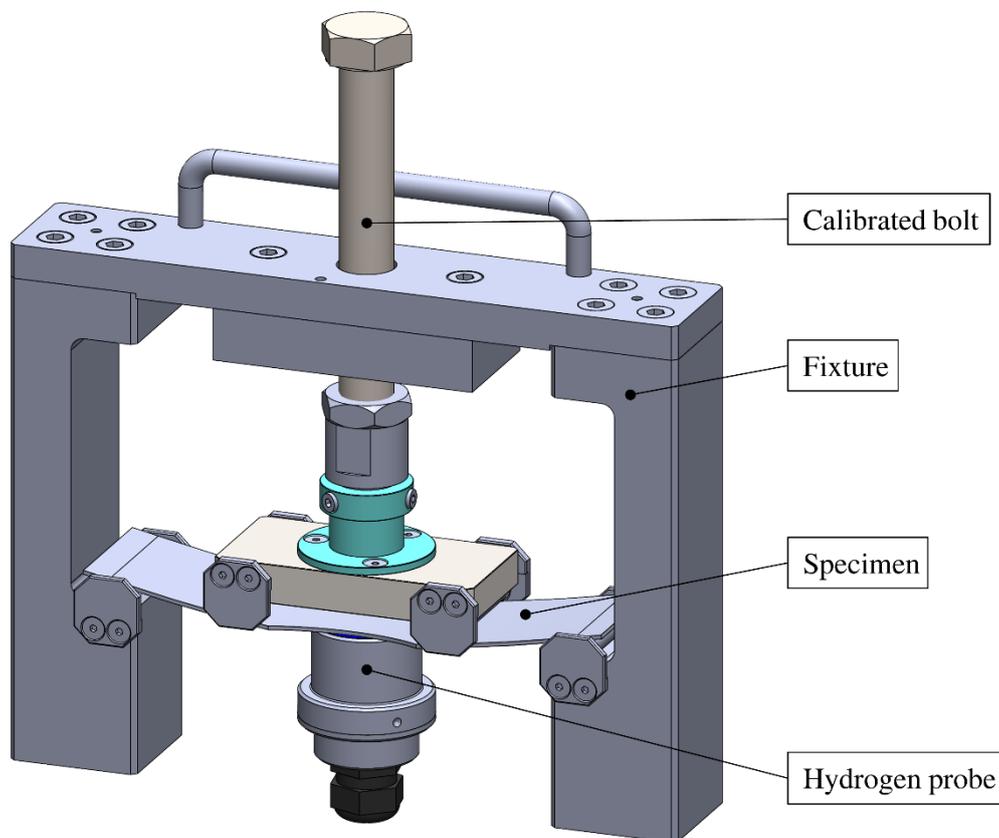
**Figure 3.** Experimental setup.

2.3. Finite Element Model

A Finite Element Model (FEM) was implemented to simulate the diffusion of the hydrogen during the test. The hydrogen migration model, presented in equation (4), was implemented in the software *Ansys Mechanical* by employing the coupled stress-diffusion migration models available in this software [16]. The hydrogen concentration is considered as a nodal degree of freedom and, as a consequence, it depends on position and time.

The material was modeled as homogenous, isotropic, linear elastic. The specimen was implemented as a 3D solid model meshed with 20 nodes hexahedral finite elements suitable for structural-diffusion coupling, Figure 13. Due to the double symmetry, only one-quarter of the specimen was modeled. In the region of the measurement, the mesh was refined in the direction of the specimen thickness by using elements having dimensions: (0.8×0.8×0.2) mm. Due to the relatively low bending stiffness of the specimen in the loading conditions, the non-linearity due to large displacements was included.

The loading fixture was modeled by a rigid body. Unilateral contact elements were used at the interface with the specimen. The external support was held in a fixed position, while a uniform displacement, in the specimen thickness direction, was applied to the internal support to model the imposed fixture displacement that produces the bending load.

A uniform initial nodal hydrogen concentration was imposed, equal to the value measured on the specimen after the hydrogen charging.
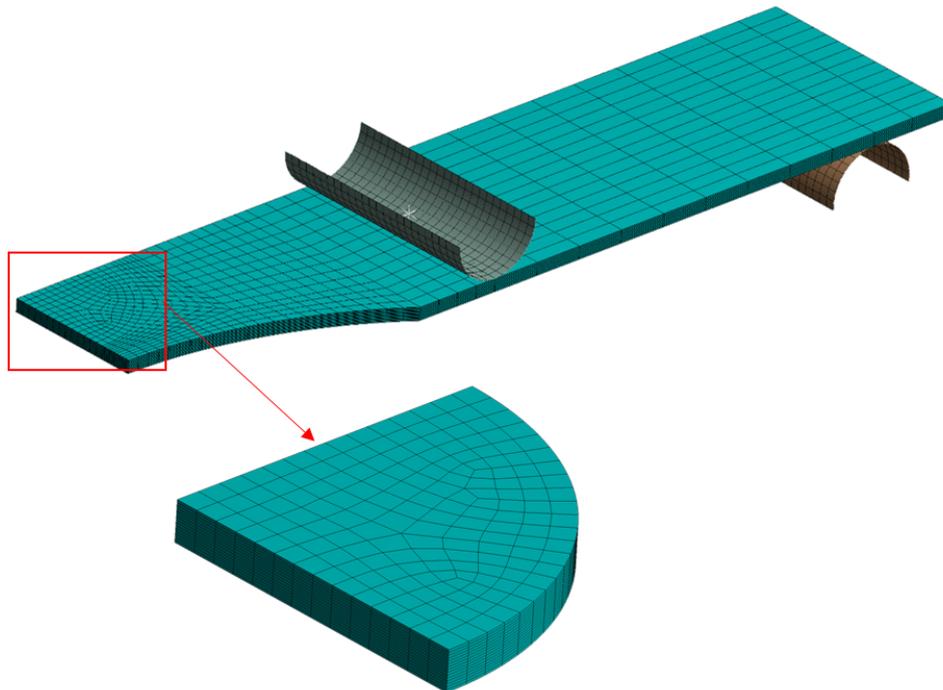
Figure 4. FEM mesh.

The interactions between the component and the environment were modeled either by imposing a specific hydrogen concentration on the surface nodes or by defining the diffusion flux on the specimen walls. In the test simulation, it was considered a specimen extracted from a sheet of high strength steel with hydrogen-impermeable coatings having a thickness of 1.2 mm by laser cutting. A null flux was consequently imposed on the coated surfaces and a condition of perfect desorption, namely null nodal concentration, was considered on the lateral surface, Figure 5. A null flux condition was also imposed on the symmetry planes.

The diffusivity of the material was considered isotropic and equal to the value obtained by standard permeation tests carried out in the thickness direction on the analyzed material at different temperatures in the range between 20°C and 30°C.
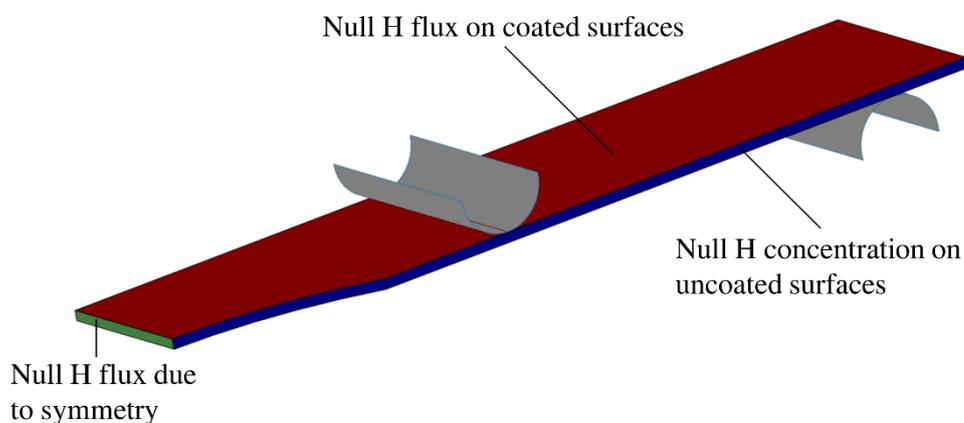

**Figure 5.** Boundary conditions for the case study.

3. Results and discussion

The test configuration demonstrated to produce a hydrostatic stress field that, in the central region of the specimen, was almost uniform on the specimen tensile surface, Figure 6. Although the maximum value of the hydrostatic stress occurred near the edge, because of the blunt notch, the in-plane stress gradient was very smooth. In the hydrogen measurement area, a 10% variation of the hydrostatic stress can be observed.

The hydrostatic stress field showed a severe and almost constant gradient in the thickness direction, due to the bending moment, Figure 7. It can be observed that the stress profile is not perfectly linear and the neutral axis does not pass through the centroid of the section, as a consequence of the significant specimen curvature produced by the applied load. In fact, to reach the desired stress level in the specimen, a displacement greater than 10 times the specimen thickness was necessary.
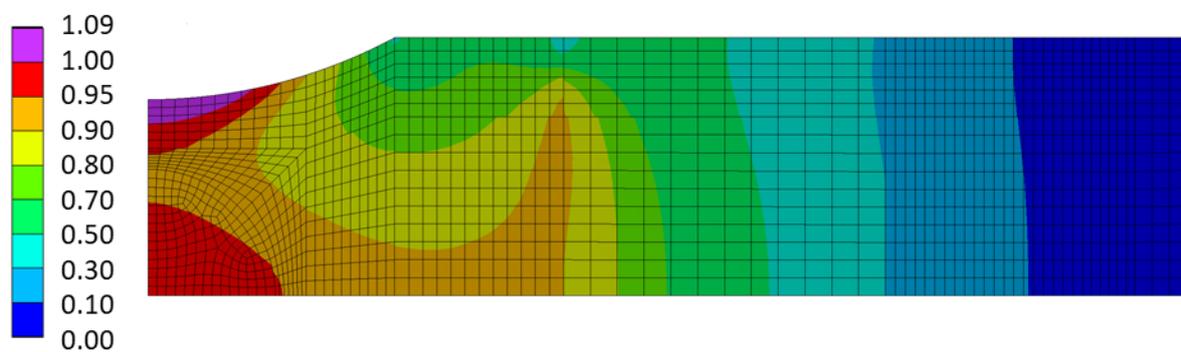
Figure 6. Hydrostatic stress distribution on the specimen tensile surface (stresses normalized with respect to the maximum value occurring in the central region).

Position in thickness direction (tensile side on the left), mm
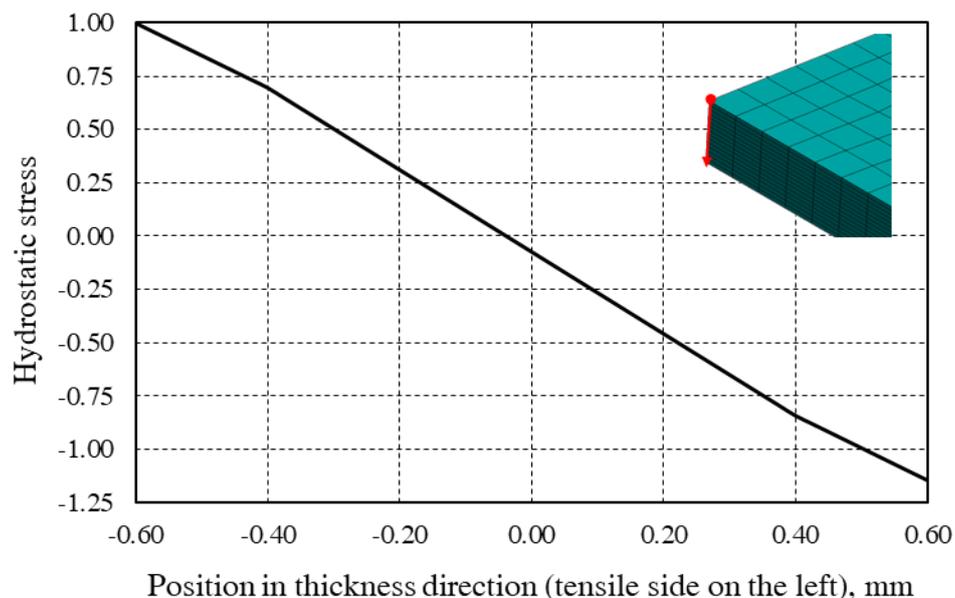
Figure 7. Hydrostatic stress distribution in the thickness direction, in the central region (stresses normalized with respect to the maximum value occurring in the tensile region).

During the test, the hydrogen migrates towards the regions affected by positive (tensile) hydrostatic stress, reaching the highest concentration in the central region of the specimen, Figure 8. After a

transient, the hydrogen distribution in the central region of the tensile surface of the specimen replicates the hydrostatic stress distribution, whilst near the edges the concentration gradient became significant due to the not coated surfaces. The hydrogen concentration in the surface exposed to the Helios IV device was almost uniform. Starting with an initial concentration of 1 ppmw, the final value in the analyzed area ranged between 1.27 and 1.31 ppmw, as showed in Figure 8. The central area of the specimen resulted to be suitable for the application of the hydrogen sensor.

In the area facing the hydrogen sensor, the concentration exhibits a monotonous increase with time, Figure 9. It can be observed that it is not useful to extend the test duration beyond 3h. However, the time depends on the amount of the applied load and the material diffusivity.

By analyzing the hydrogen concentration profile in the specimen thickness, it can be observed that, during the test, the hydrogen migrates from the compressed side to the tensile side of the specimen, Figure 10. The stress-driven migration is significant only in the central part of the specimen and the flux in the plane directions (neglecting the border regions) can be neglected even for a test duration of several hours.
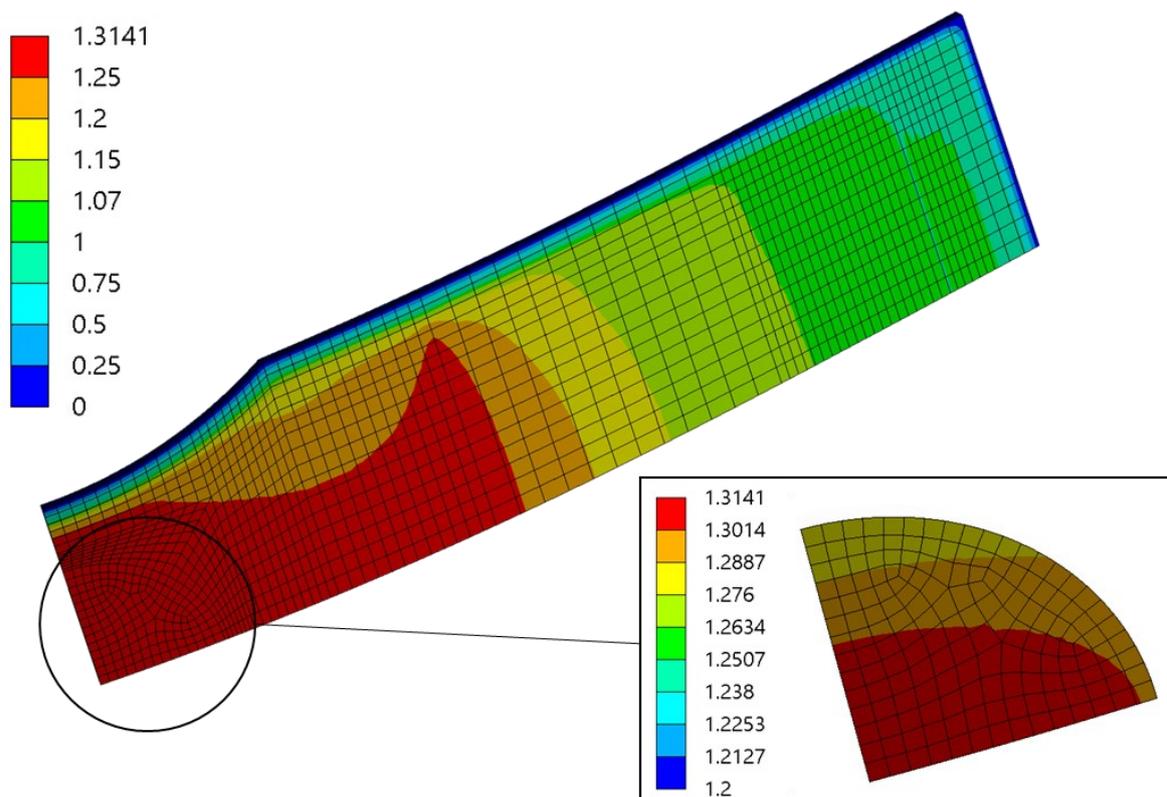
Figure 8. Hydrogen concentration on the tensile side of the specimen at the end of the test, simulation ran starting from a uniform initial concentration of 1 ppmw.
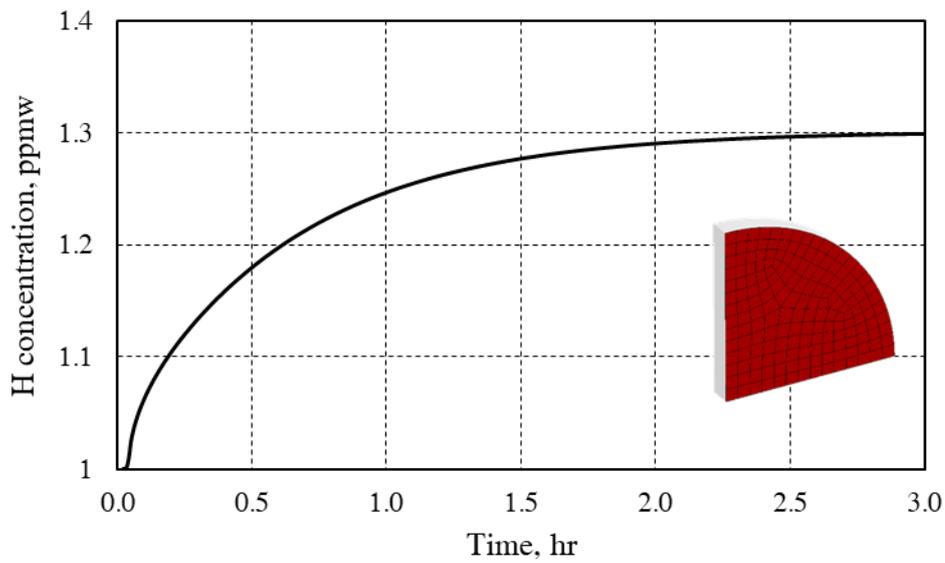
Figure 9. Evolution of the hydrogen concentration on the surface facing the probe, during the mechanical test.
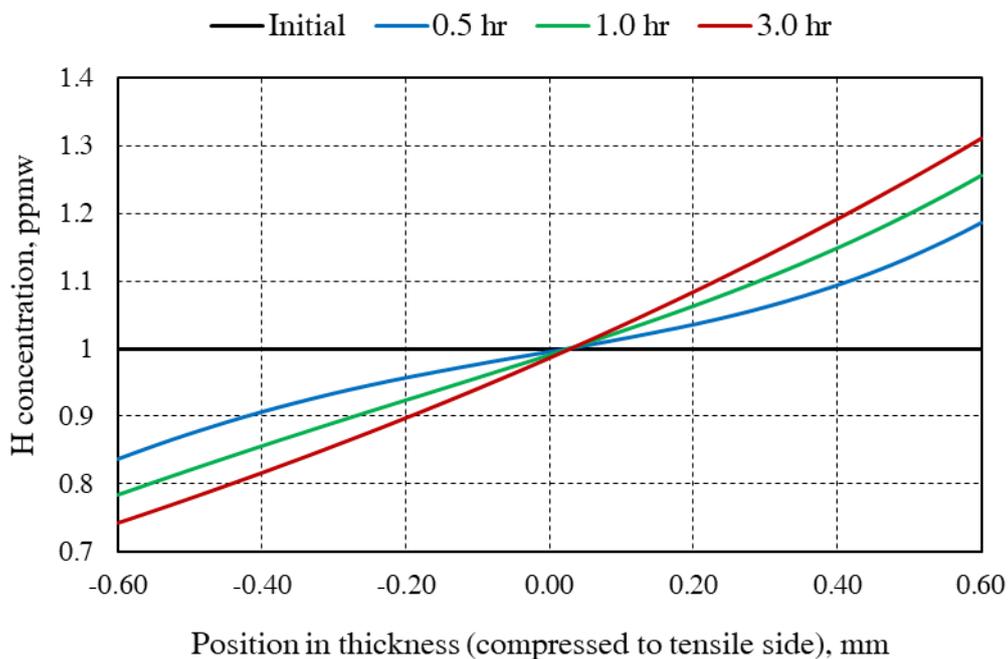

Figure 10. Hydrogen concentration versus in-depth position in the central region of the specimen, calculated for increasing dwell times.

Increments in the applied load and, consequently, in the tensile stress, as long as within the limit of the elastic behavior, significatively increases both the hydrogen flux and its concentration in the area facing the sensor, Figure 11.

The test showed a limited sensitivity to variations of the material diffusivity caused by changes in the room temperature. As shown in fig. 11, a variation of the room temperature in the range between

20°C and 30°C affects the concentration growth rate but not the value of the hydrogen concentration at the saturation condition in the measurement area.
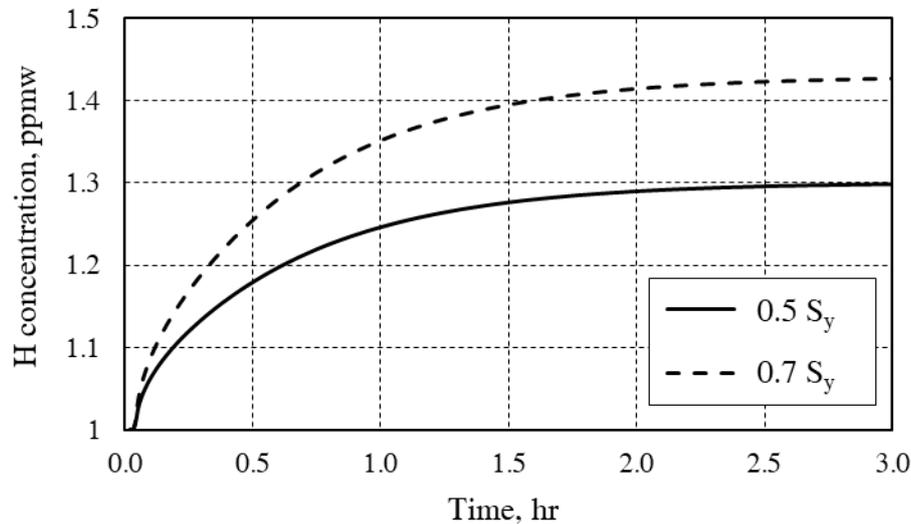
Figure 11. Hydrogen concentration on the surface facing the probe during the test with different maximum tensile stresses applied to the specimen (Sy: Yield strength).
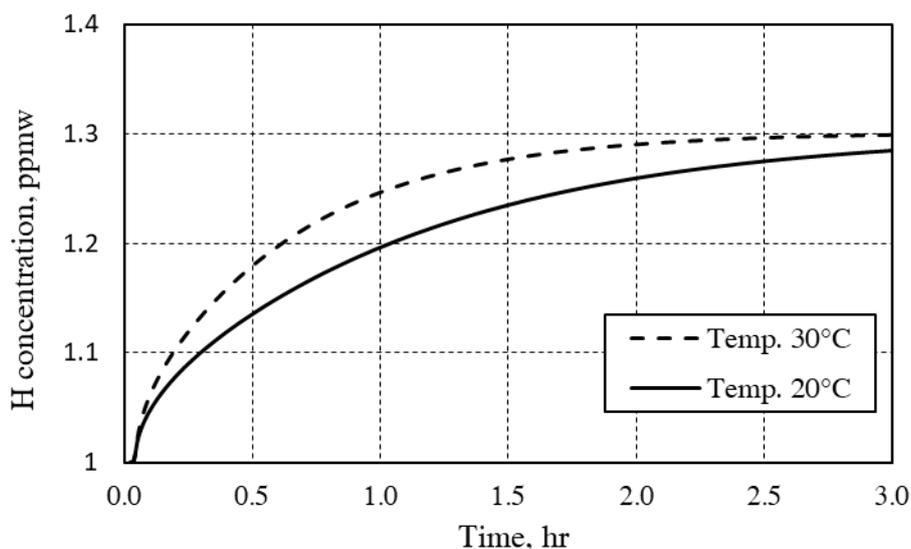
Figure 12. Sensitivity of the measured quantity to the test temperature.

4. Conclusions

A test configuration suitable for effective validation of hydrogen diffusive models which include the principal phenomena governing the process into stressed mechanical components was presented.

The mechanical configuration resulted to be effective in producing a controllable and in-plane uniform hydrostatic stress gradient, aimed at generating a uniform hydrogen concentration in the measurement area. The configuration was tailored for local measurement of the hydrogen concentration in the proximity to the surface of the specimen affected by tensile stress due to bending, thus avoiding

the necessity to average the concentration on a wide volume. These two factors meet the requirements for a test configuration necessary for validating a hydrogen diffusive model.

A Finite Element, implemented in the software *Ansys Mechanical* and developed to include all the principal phenomena affecting the hydrogen diffusion into stressed components, was used to simulate the test and evaluate the sensitivity to the parameter variations.

Acknowledgments

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