Hydrogen Embrittlement in Metals: Analysis of Directionality of Hydrogen Diffusion Assisted by Stress and Strain

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Abstract Hydrogen diffusion within a metal or alloy is conditioned by the stress-strain state therein. For that reason it is feasible to consider that hydrogen diffuses in the material obeying a Fick type diffusion law including an additional term to account for the effect of the stress state represented by the hydrostatic stress. According to this law hydrogen diffuses not only to the points of minimum concentration (driven by its gradient), but also to those of maximum hydrostatic stress (driven by its gradient), the diffusion itself being also conditioned by the gradient of plastic strain. In this paper the hydrogen transport by diffusion in metals is modelled in notched specimens where loading generates a triaxiality stress state. To this end, two different approaches of stress-assisted hydrogen diffusion, one-dimensional (1D) and two-dimensional (2D), were compared in the vicinity of the notch tip in four notched specimens with very distinct triaxiality level at two different loading rates. The 2D approach predicts lower values of hydrogen concentration than the 1D approach, so that a *loss of directionality* of hydrogen diffusion towards the location of highest hydrostatic stress appears in the 2D case. This loss of directionality of hydrogen diffusion depends on both notch geometry parameters (radius and depth) and loading rate (or straining rate).

Keywords Hydrogen diffusion, Numerical models, Notched samples, Directionality of diffusion.

1. Introduction

Catastrophic fracture of structural materials in harsh environments for lower loading level than in air is caused many times by hydrogen diffusion towards material lattice and accumulation in certain places where damage at microstructural level is produced [1-4]. This phenomenon, known as *hydrogen embrittlement* (HE) or *hydrogen-assisted fracture* (HAF), has a key role in prestressed concrete structures due to the high susceptibility of the prestressing steel to this type of fracture [5-7]. At the critical fracture instant, the hydrogen concentration C reaches a critical value C_{cr} in a certain material locus $\vec{x}_{cr}$. The critical value of hydrogen concentration depends on the stress-strain state at the critical instant in the critical place or prospective location for fracture initiation [8]. Thus, the fracture criterion can be expressed as follows:

$$C_{cr} = C_{cr}(\sigma_i, \varepsilon_i) \text{ in } \vec{x} = \vec{x}_{cr}, \tag{1}$$

where $\vec{x}$ is the spatial vector coordinates. In this equation the influence of the stress-strain state on the critical value of hydrogen concentration is included by means of both tensor invariants represented by the principal stresses, σ_i, and principal plastic strains ε_i (i = 1, 2, 3).

To study this phenomenon, constant-extension-rate tensile (CERT) tests in a hydrogenating environment are commonly used. The mechanical load applied during the test generates a certain stress-strain state in the material according to the geometry of the tested specimen. Although specimens for this type of test could exhibit different shapes, diverse studies [9,10] consider round notched bars as the best suited to the evaluation of these fracture phenomena. Obviously, under CERT test load conditions the stress and strain state varies with time and, consequently, a transient analysis of the hydrogen diffusion must be carried out.

The analysis of the HAF process presents a serious difficulty: the experimental determination of the value of hydrogen concentration $C(\vec{x},t)$ at certain point, $\vec{x}$, for a given time t. This difficulty becomes particularly important in the analysis of HAF process for critical conditions, C_{cr} = $C(\vec{x}_{\mathrm{cr}},t_{\mathrm{cr}})$. To solve this objection is essential (i) to find the HAF focus by means of metallographic techniques of the fractured specimens analysis [9,11,12], and (ii) to determine the local values of the variables governing the diffusion process, i.e., hydrogen concentration C, the hydrostatic stresses σ_{i} and equivalent plastic strains $\varepsilon_{\mathrm{i}}^{P}$ (i = 1,2,3).

The mechanical variables representing the stress-strain state in the hydrogen diffusion model can be obtained by numerical simulation revealing the evolution of stress-strain state in the notched specimen during CERT test. Unfortunately, nowadays an advanced numerical simulation code of general use that solves the problem stated in this paper is not available: the analysis of transient hydrogen diffusion assisted by stresses considering a 2D approach. To overcome this difficulty, the hydrogen concentration at any place and time of the transient diffusion assisted by stress state can be obtained by means of an *ad hoc* numerical code based on the finite element method (FEM) developed by the authors [13]. With the help of this tool the analysis of the time evolution of hydrogen concentration can be developed in the notched samples considered in this study during the CERT tests performed under different extension rates. The numerical simulations were carried out taking into account both approaches of the hydrogen diffusion assisted by stress state: *one-dimensional* (1D) and *two-dimensional* (2D). The differences between both simulations reveal a loss of directionality of hydrogen diffusion into metal.

2. Problem Statement

The numerical modelling of this problem raises a huge complexity due to the following fact: the hydrogen diffusion equation must consider the stress field generated by the remote load applied during CERT test. In general terms hydrogen diffusion in metals obeys a Fick type diffusion law including an additional term to account the effect of the stress state, which is time dependent, i.e. transient for the analyzed cases. Thereby, the stress-assisted diffusion flux of hydrogen is:

$$\boldsymbol{J} = D\nabla C + D\frac{V_{\mathrm{H}}}{RT}C\nabla\sigma, \tag{2}$$

where D is the diffusion coefficient, V_{H} the molar partial volume of hydrogen in metal, R the ideal gases constant and T the absolute temperature.

The role of stress in hydrogen diffusion is commonly associated with one of the stress tensor invariants: the hydrostatic stress (or mean normal stress) σ. The relevance of stress in hydrogen transport by diffusion and HAF is well known from previous references [14-16], and, according to Eq. (2) is established that hydrogen diffuses not only to the points of minimum hydrogen concentration C (driven by the gradient of concentration), but also to the sites of maximum hydrostatic stress σ (driven by the gradient of stresses) [17]. So, the hydrogen diffusion process assisted by stress in non-homogeneous stress fields can be expressed as follows [8]:

$$\frac{\partial C}{\partial t} = D\left(\nabla^2 C - \frac{V_{\mathrm{H}}}{RT}\nabla C\nabla\sigma - \frac{V_{\mathrm{H}}}{RT}C\nabla^2\sigma\right). \tag{3}$$

i.e., a parabolic-type partial differential equation given in terms of hydrogen concentration C and hydrostatic stress s as the relevant variables of the process od hydrogen transport.

Free of hydrogen specimens before the test were considered and, consequently, the initial condition of null hydrogen concentration at the initial time ($C(\vec{x},t)|_{t=0} = 0$) was applied in simulations. The material considered in this study is a hot rolled bar of eutectoid pearlitic steel (C 0.75%, Mn 0.67%, Si 0.200%, P 0.009%, S 0.009%, Cr 0.187%, V 0.053%), whose mechanical properties are: Young´s modulus 195 GPa, Yield Strength 720 MPa and ultimate tensile strength (UTS) 1270 MPa.

Finally the values of relevant parameters of metal-hydrogen interaction were obtained from previous works [18,19] as D = 6.6 10^{-11} m^2/s y V_H = 2 10^{-6} m^3/mol. The geometry of a round notched specimen can be defined by two parameters (Table 1): the notch tip radius ρ and notch depth a. To have results independent of sample dimensions these parameters were normalized with the specimen diameter d (where d = 12 mm for all the notched geometries analyzed in this study).

Table 1. Notch parameters of the analyzed notched specimens

Parameter	**A**	**B**	**C**	**D**
ρ/d	0.03	0.05	0.40	0.40
a/d	0.10	0.30	0.10	0.30

Fig. 1 shows a scheme of the four analyzed notched specimens, including the corresponding notation used to identify each one. To analyze the effect on hydrogen diffusion of the extension rate during the CERT tests, two different values were considered: fast extension rate, 0.1 mm/min, and slow extension rate, 0.001 mm/min.

Two numerical approaches of hydrogen diffusion model, based in previous research [13,20], are used in present work: the *one-dimensional approach* (1D) and the quite more realistic (although time-consuming) *two-dimensional approach* (2D). Transient stress state generated in the specimen by remote loading during CERT test is included as input data in the FEM code developed *ad hoc* for both simulations of diffusion process. The specimen stress state is obtained from a previous mechanical simulation of the CERT test with a commercial FEM code considering small-strain. The same stress field was considered in the two approaches (1D and 2D) used in this paper.

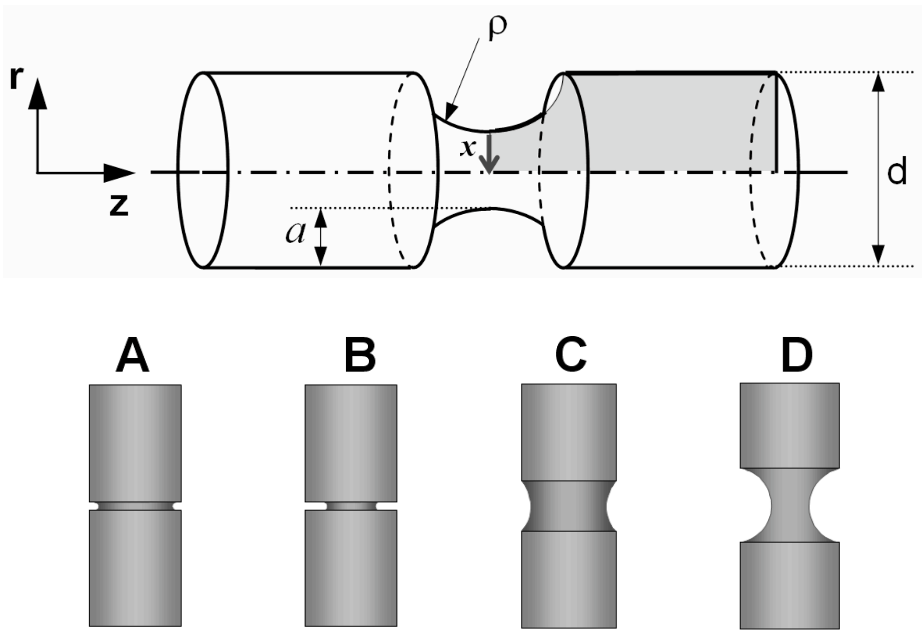

Fig. 1. Scheme of the notched specimens and parameters used for describing the notch

The 1D approach considers hydrogen diffusion is exclusively developed in radial direction (r), i.e., through the wire radius placed at notch symmetry plane. However, in 2D approach the hydrogen diffusion proceeds in both radial (r) and axial direction (z). Therefore, differences in the hydrogen concentration given by the two considered approaches can be associated to a *geometric factor*. The FEM simulation of the hydrogen diffusion assisted by stresses was performed with linear elements for both approaches (1D and 2D).

In these simulations the exposure time to harsh environment was chosen equal to the fracture time (t_f) obtained in the study [21], where similar specimens –material and notched geometries– were tested in an inert environment (air). This way, data related to fracture time due to HAF (t_{HAF}) are included in the results of the simulation performed since $t_{HAF} < t_f$ [12].

The results of the displacement at fracture instant, u_f(A) = 0.4 mm, u_f(B) = 0.13 mm, u_f(C) = 1.2 mm and u_f(D) = 0.42 mm, obtained in [21] with an extensometer of 25 mm gage length, were used to determine the time of fracture in air (t_f) according to the following relation $t_f = u_f/\dot{u}$ for each one of the two considered extension rates $\dot{u}$ (0.1 and 0.001 mm/min).

3. Numerical Results

The hydrogen accumulation in the material is represented by the relative hydrogen concentration C_r ($C_r = C/C_0$), which can be defined as the hydrogen concentration normalized with the equilibrium hydrogen concentration in a virgin material C_0, i.e., free of stress and strains. Fig. 2 shows the distribution of the relative hydrogen concentration (C/C_0) through the considered notch symmetry plane for a diffusion time lower than the fracture time in air (t_f) obtained for each one of the two extension rates considered, 0.1 mm/min and 0.001 mm/min.

As can be shown in Fig. 2 two different trends were obtained according to the extension rate: on one hand, for the highest extension rate of 0.1 mm/min (Fig. 2 left) slightly differences appear in hydrogen concentration obtained by 1D and 2D approaches of diffusion model. On the other hand, when the lowest extension rate of 0.001 mm/min is applied (Fig. 2 right) a clear influence of the geometric factor on hydrogen diffusion is revealed, especially, in the notched geometry type A where high differences in relative hydrogen concentration are obtained considering 1D and 2D approaches. Therefore the use of 1D approach (less realistic than 2D approach) leads to a loss of accuracy in the determination of relative hydrogen concentration, it being more accused for low extension rate tests and sharp notches.

According to these results hydrogen diffuses not only through the notch symmetry plane but also towards other directions. However, most of hydrogen is preferentially accumulated in the radial notch symmetry plane direction, as could be expected since H diffuses towards the location where the highest hydrostatic stress appears (situated in the notch symmetry plane [13]). So, according to Fig. 2, the lower the extension rate the more accused the effect of the *geometric factor* on hydrogen diffusion, it becoming inappreciable for high extension rate test where the hydrogen diffusion is performed practically through the notch symmetry plane with a negligible *loss of directionality*.

The influence of geometric factor on hydrogen diffusion is dependent of notch geometry parameters (radius and depth). So, the influence of this factor is lower for blunt notched samples with a high notch radius (notches C and D) than for sharply notched geometries (notches A and B) with a low notch radius (Fig. 2). According to that, a stronger influence of the geometric factor on hydrogen diffusion appears for high values of the depth (distance) from the notch tip (x).

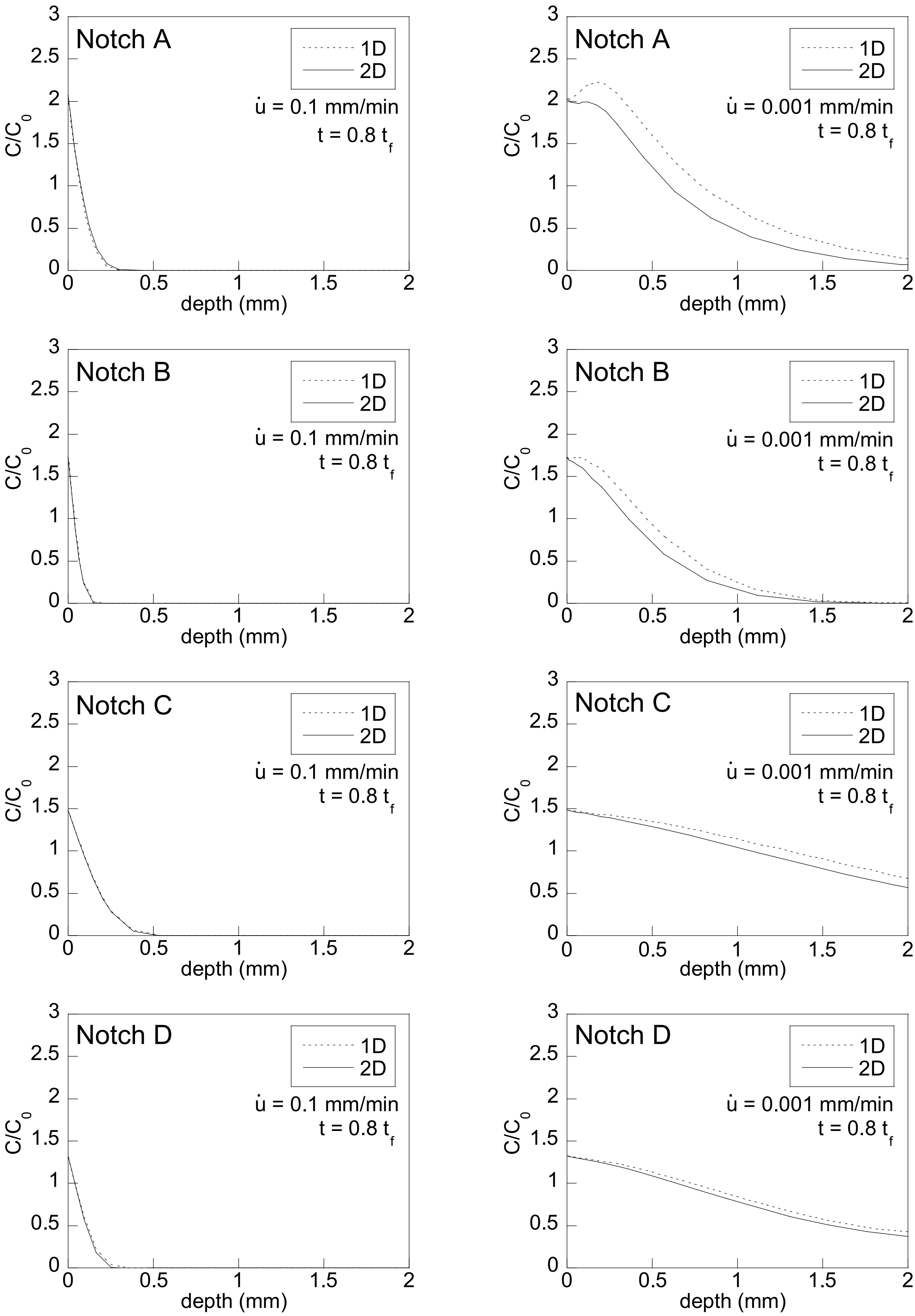

Figure 2. Distribution of hydrogen concentration through the notch symmetry plane for the geometries analyzed and an extension rate of 0.1 mm/min (left) and 0.001 mm/min (right) at exposure time $t = 0.8t_f$

The loss of accuracy of 1D approach with regard to the more realistic 2D approach can be quantitatively estimated by a new parameter λ defined as the amount of diffused hydrogen out of the notch geometry plane, thus, λ represents the *loss of hydrogen diffusion directionality:*

$$\lambda = \frac{C_{\mathrm{r}}(\mathrm{1D}) - C_{\mathrm{r}}(\mathrm{2D})}{C_{\mathrm{r}}(\mathrm{1D})}. \qquad (4)$$

As a sketch, the 1D approach could be considered as a hollow cylindrical tube through hydrogen diffuses and the 2D approach could be considered as a hollow cylindrical tube with small holes placed in the cylinder walls. So, in first case (1D approach) a fluid that flows inside the cylinder is trapped inside it and is not able to pass through the cylinder walls whilst in second case (2D approach) the fluid can escape out of the cylinder through the holes causing a loss of fluid flux in relation to the first case.

To get a clear view of the influence of the parameters defining the different notched geometries on the loss of directionality, in Fig. 3 the distribution of the parameter through the notch symmetry plane is represented for each one of the four notched geometries simulated under the lowest loading rate, 0.001 mm/min, for a exposure time to harsh environment of 80% of the time to fracture in air, $t = 0.8\ t_{\mathrm{f}}$. Fig. 3 shows a common trend for notched wires with the same notch tip radius, ρ. For blunt geometries with a higher notch radius (notches C and D) a low loss of directionality is obtained, i.e., the loss of accuracy of the 1D approach is low, cf. Fig. 2, whereas for sharp notches with a low notch radius (notches A and B) the 2D approach is required to obtain an adequate simulation.

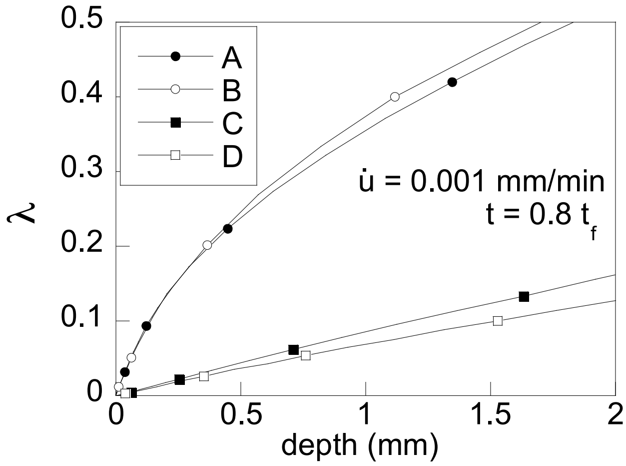

Figure 3. Distribution of loss of hydrogen diffusion directionality, through notch symmetry plane for the four notched geometries simulated under an extension rate of 0.001 mm/min at diffusion time $t = 0.8t_f$

According to these results, the notch tip radius (ρ) is the parameter governing the amount of hydrogen available for diffusing toward points out of notch symmetry plane in axial direction, with a second order effect of the notch depth (a). Fig. 4 shows a scheme of the diffusion path followed by hydrogen inside the material as a function of the dimensional approach (1D or 2D) to the process of hydrogen diffusion in the solid.

The reason why hydrogen diffuses toward the axial direction out of the notch symmetry plane can be attributed to the key role that stress state plays in the hydrogen diffusion assisted by stress model (Eq. 3). According to this model, hydrogen diffuses to the places where the maximum hydrostatic stress appears [17]. In the case of 1D approach these points are placed inside the notch symmetry plane, which means that hydrogen diffuses exclusively inside that plane. However, in the case of 2D approach, the maximum hydrostatic stress σ appears over a *zone* [13] allowing hydrogen to move towards diverse places. Fig. 3 shows a null loss of hydrogen diffusion directionality in points near the notch tip. The same figure indicates that the deeper is the considered point the higher is the loss of directionality, which is represented in the scheme shown in Fig. 4.

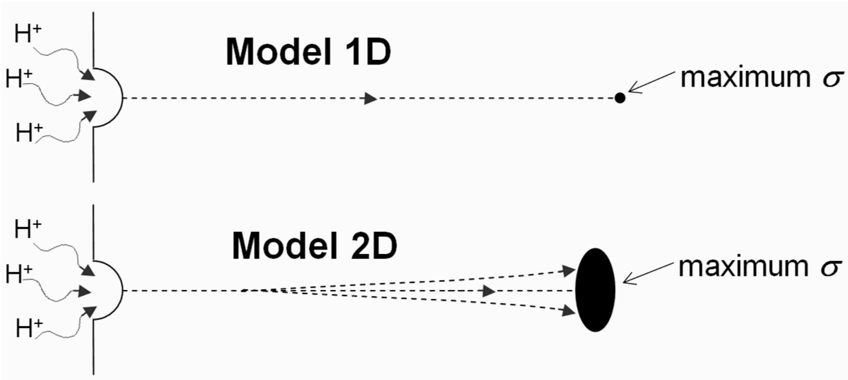

Figure 4. Scheme of hydrogen diffusion path inside a material taking into account the diffusion model approaches considered in numerical simulations.

4. Conclusions

- For high loading rates the hydrogen concentration predicted by the 1D approach to hydrogen diffusion in the material is practically equal to that predicted by the 2D approach, and therefore the influence of the *geometric factor* is not significant.
- For low loading rates during the constant extension rate tensile (CERT) tests the loss of accuracy of results obtained with the 1D approach to hydrogen diffusion in the material becomes more significant due to the loss of directionality in diffusion path.
- During the CERT tests, certain amount of hydrogen diffuses towards points placed out of the notch symmetry plane. This supposes a *loss of hydrogen diffusion directionality* in relation to the radial path obtained in 1D approach.
- The loss of directionality of hydrogen diffusion is more accused for low extension rates during the CERT tests and points placed far away from the notch tip, it becoming more significant in sharp notches with low notch radius.
- Obtained results reveal that the notch tip radius (sharp or blunt notched geometries) is the most relevant geometric parameter governing the loss of directionality of hydrogen diffusion, the notch depth exhibiting minor importance.
- Hydrogen diffusion toward points placed out of the notch symmetry plane is strongly dependent on the distribution of hydrostatic stress inside the material. In the 1D approach the maximum hydrostatic stress location is a single point, whereas in the 2D approach it is a zone.

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