Hydrogen embrittlement mechanisms in metals: a modelling approach

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Abstract: *It is well known that high strength steels are tremendously affected by hydrogen. The aim here is to provide a modelling of the HELP (Hydrogen Enhanced Local Plasticity) mechanism fully coupled with the hydrogen transport equation. The hydrogen diffusion equation is implemented in a UMATHT subroutine by considering similarities between the heat and mass diffusion equations. A coupled temperature-displacement procedure has been adopted to allow the coupling between hydrogen diffusion and the mechanical behaviour of the material.*

Keywords: *Hydrogen embrittlement, Constitutive models, hydrogen diffusion equation, UMATHT.*

1. Introduction

Experimental studies and fractography analysis of high strength steels indicate a deleterious influence of hydrogen on the constitutive response. The idea is to model combined HELP (Hydrogen Enhanced Local Plasticity) and HID (Hydrogen Induced Decohesion) mechanisms (Sofronis, 1989; Robertson, 1999; Robertson, 1986) in which the hydrogen content is evaluated by solving the hydrogen diffusion equation (McNabb, 1963; Oriani, 1978). Previously we have analysed a carbides-rich region in dissimilar weld (Barrera, 2013; Barrera, 2014). An ABAQUS finite element model of the microstructure was created by converting a TEM image.

The presence of fine carbides plays an important role in the constitutive response of these materials. Simulations of the response of similar materials show that in regions where the hydrogen content is high the matrix surrounding the carbides softens and plastic flow is localized. Moreover, the presence of hydrogen lowers the cohesive strength, giving rise to microcrack formation at the carbide- matrix interface, leading to microvoid formation. As deformation proceeds the pores enlarge and link to form cracks, which generates the failure surface. The interface between the carbides and the surrounding metal matrix is represented by cohesive elements. A user cohesive element (UEL) has been coded incorporating a traction separation law

which is a function of local hydrogen content and of plastic strain which also accounts for the development of dislocation structures at the carbides. The behaviour of the matrix was modelled by a hardening law that depends on the local hydrogen content via a UMAT, and a simple linear distribution of hydrogen was used. Here we ignore the presence of the carbides. We then model the constitutive behaviour of the matrix whose hardening law is function of the hydrogen content evaluated by solving the diffusion equation. The hydrogen diffusion equation is implemented in a UMATHT subroutine by considering similarities between heat and mass diffusion equations. A coupled temperature-displacement procedure has been adopted to allow the coupling between hydrogen diffusion and the mechanical behaviour of the material.

2. Hydrogen diffusion equation

It is well known that hydrogen being the smallest element diffuses more easily through metals than any other element. Even at low concentration hydrogen often leads to the embrittlement of metals for reasons that are not yet well understood but are certainly related to the speed at which it can diffuse to highly stressed regions.

Hydrogen atoms move through the metals by normal interstitial site (NILS) diffusion or dislocation transport. Hydrogen atoms reside either at NILS or at trapping sites such as: dislocations, grain boundaries, carbide/matrix interface, microvoids and other defects (see Figure 1). The vast majority of sites are the normal sites NILS and the minor fraction of the sites are the trapping sites. Here we consider a lattice consisting of two kinds of sites for occupancy by hydrogen. The hydrogen atoms in the normal sites are denoted C_L and the hydrogen atoms trapped at the dislocations are denoted C_T. Hydrogen trapping at defects has a large effect on its diffusion in solids of solute. Hydrogen diffuses so easily that even shallow traps can produce a significant effect on the diffusivity. One of the first theories on the mobility of dissolved hydrogen in an iron lattice containing trapping sites was given by McNabb and Foster (McNabb, 1963). They introduced a diffusion equation solved with terms for sources and sinks. Oriani (Oriani, 1978) reformulated the work by McNabb and Foster introducing the assumption of local equilibrium between the mobile and the trapped populations for a restricted domain of degree of trap coverage. Mass conservation states that the changing rate of the total hydrogen in the volume Ω is equal to the flux through the surface Γ:

$$\frac{\partial}{\partial t}\int_{\Omega}\left(C_L + C_T\right)d\Omega + \int_{\partial\Omega} J \cdot n dS = 0 \tag{1.1}$$

The driving force for diffusion is the chemical potential gradient:

$$J = -\frac{D_L C_L}{RT}\nabla\mu \tag{1.2}$$

Where D_L is the diffusion coefficient of hydrogen and μ is the chemical potential defined as follows:

$$\mu = \mu_0 + RT\ln C_L + \mu_\sigma \tag{1.3}$$

μ_0 denotes the chemical potential at standard condition. μ_σ Is the chemical potential function of stress:

$$\mu_\sigma = -\frac{\sigma_{kk}}{3}\overline{V_H} \tag{1.4}$$

and $\sigma_H = \frac{\sigma_{kk}}{3}$ the hydrostatic stress and $\overline{V_H}$ the is the partial volume of hydrogen in solid solution. Substituting eq. (1.3) into eq. (1.2) we can express the flux as follows:

$$J = \frac{D_L C_L \overline{V}_H}{RT}\nabla\sigma_H - D_L\nabla C_L \tag{1.5}$$

Now substituting eq. (1.5) into eq. (1.1) we obtain the following equation:

$$\frac{\partial}{\partial t}\int_\Omega \left(C_L + C_T\right)d\Omega + \int_{\partial\Omega}\left(\frac{D_L C_L \overline{V}_H}{RT}\nabla\sigma_H - D_L\nabla C_L\right)\cdot n dS = 0 \tag{1.6}$$

By applying the divergence theorem eq. (1.6) becomes:

$$\frac{\partial C_L}{\partial t} + \frac{\partial C_T}{\partial t} - \nabla\left(D_L\nabla C_L\right) + \nabla\left(\frac{D_L C_L \overline{V}_H}{RT}\nabla\sigma_H\right) = 0 \tag{1.7}$$

Now Oriani's theory assumes that the trapped hydrogen population is in equilibrium with the population upon normal lattice sites not only in the static case but also during diffusion. We denote the fraction of the available sites occupied by the population in NILS as ϑ_L and ϑ_T the

site fraction occupied by the trapped population. The equilibrium between the two populations can be described by introducing the equilibrium constant *K* given by $K = \frac{\alpha_L}{\alpha_T}$ where $\alpha_L = \frac{\vartheta_L}{1-\vartheta_L}$ and $\alpha_T = \frac{\vartheta_T}{1-\vartheta_T}$ are the activities of the hydrogen upon the normal lattice sites and the trapping sites. Considering that the situation that Oriani considered was that $\vartheta_L \ll 1$ it is possible to express the equilibrium constant *K* as follows:

$$K = \frac{1}{\vartheta_L}\frac{\vartheta_T}{1-\vartheta_T} \tag{1.8}$$

Now $C_L = \vartheta_L N_L$, $C_T = \vartheta_T N_T$, where N_L, N_T are the numbers of atoms in NILS and in the traps respectively.

It can be derived that:

$$\frac{\partial C_T}{\partial C_L} = \frac{C_T\left(1-\vartheta_L\right)}{C_L} \tag{1.9}$$

Sofronis and McMeeking (Sofronis, 1989) formulated the hydrogen transport problem coupled with large deformation elastic-plastic behaviour of a material based on Oriani's theory. In (Sofronis, 1989) the authors incorporated the effect of hydrostatic stress and trapping site. In this model they assume that hydrogen atoms diffuse through lattice sites and that trap sites are filled by lattice diffusion. These trap sites are formed due to plastic deformation. Krom et al. (Krom, 1999) demonstrated that the hydrogen transport model proposed in (Sofronis, 1989) does not provide a correct hydrogen balance. Hence in (Krom, 1999) a modification on the hydrogen diffusion model is introduced which includes a factor depending on the strain rate. The strain rate factor decreases the hydrogen concentration in lattice sites due to the filling of trap sites. As results of this the modified hydrogen transport model predicts a strong dependence of the hydrogen concentration in lattice sites on the strain rate, instead the hydrogen concentration in the trap sites is not significantly affected.

$$C_T = \vartheta_T N_T\left(\dot{\varepsilon}_p\right) \tag{1.10}$$

Considering eqns. (1.9) and (1.10), the term $\frac{\partial C_T}{\partial t}$ in eq.(1.7) can be expressed as follows:

$$\frac{\partial C_T}{\partial t} = \frac{\partial C_T}{\partial C_L}\frac{\partial C_L}{\partial t} + \frac{\partial C_T}{\partial N_T}\frac{\partial N_T}{\partial \varepsilon_P}\frac{\partial \varepsilon_P}{\partial t} \tag{1.11}$$

Substituting eq.(1.9) into eq. (1.11) we obtain:

$$\frac{\partial C_T}{\partial t} = \frac{C_T\left(1-\vartheta_L\right)}{C_L}\frac{\partial C_L}{\partial t} + \frac{\partial C_T}{\partial N_T}\frac{\partial N_T}{\partial \varepsilon_P}\frac{\partial \varepsilon_P}{\partial t} \tag{1.12}$$

Substituting eq. (1.12) into eq. (1.7) we obtain the hydrogen diffusion equation finalized by (Krom, 1999) :

$$\frac{C_L + C_T\left(1-\vartheta_T\right)}{C_L}\frac{\partial C_L}{\partial t} - \nabla\cdot\left(D_L\nabla C_L\right) + \nabla\cdot\left(\frac{D_L C_L \overline{V}_H}{RT}\nabla\sigma_H\right) + \vartheta_T\frac{\partial N_T}{\partial \varepsilon_P}\frac{\partial \varepsilon_P}{\partial t} = 0$$

(1.13)

Where $D_{eff} = \dfrac{C_L + C_T\left(1-\vartheta_T\right)}{C_L}$ represents the effective diffusivity.

Eq.(1.13) has been implemented in a UMATHT by using the similarity between the diffusion equation and the heat equation. This is shown in the next paragraph.

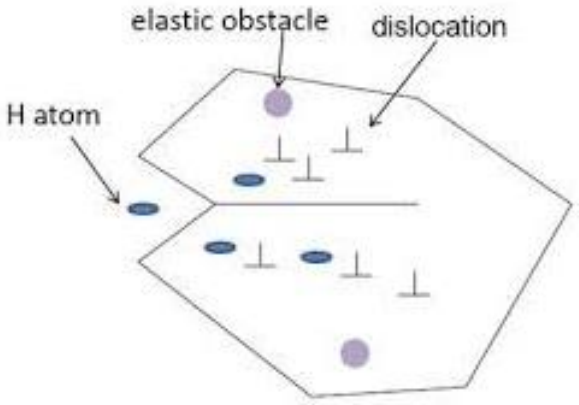

Figure.1. Hydrogen atoms reside either at NILS or at trapping sites such as: dislocations, grain boundaries, carbide/matrix interface, microvoids and other defects

3. Analogy with the heat equation

In order to implement the coupled hydrogen transport equation given in equation (1.13) we use the similarities with the heat equation as done by Chang-Sik OH et al. (OH, 2010). The coupled thermo-mechanics procedure (available in Abaqus) is used to solve coupled diffusion-mechanics problems. In Chang-Sik OH et al. (OH, 2010) the evaluation of the gradient of hydrostatic stress inside the element was calculated by storing the component of hydrostatic stress (evaluated at each gauss point) in an external file that was then read inside the UMAT and passed to the UMATHT. Here we show that we can compute directly the gradient of hydrostatic stress inside the UMATHT by using the subroutines USDFLD and GETVRM avoiding other cumbersome steps. Here we report all the details necessary to fully understand the procedure. Table 1 summarizes the analogy between the heat equation and the hydrogen diffusion equation. It can be seen that the form of the equations are similar. The degree of freedom in the heat equation is temperature: T whereas in the mass diffusion equation is the concentration of hydrogen at NILS C_L. We can write the expressions of the terms appearing in the mass diffusion equation (1.13) as shown in Table 1.

Table 1. Analogy between heat equation and diffusion equation.

HEAT EQUATION	MASS DIFFUSION EQUATION
$\rho c_P \frac{\partial T}{\partial t} + \vec{\nabla}\vec{J}_q + r_q = 0$	$\frac{\partial C}{\partial t} + \vec{\nabla}\vec{J}_m + r_m = 0$
Thermal energy per unit mass $\dot{U}_q = c_P \frac{\partial T}{\partial t}$	Chemical potential per unit mass $\rho\dot{U}_m = \frac{\partial C}{\partial t} = \frac{\partial\left(C_L + C_T\right)}{\partial t}$
Degree of freedom: temperature T	Degree of freedom: concentration C_L
Heat flux: $\vec{J}_q$	hydrogen flux: $\vec{J}_m = \frac{D_L C_L \overline{V}_H}{RT}\vec{\nabla}\sigma_H - D_L\vec{\nabla}C_L$
Heat source: r_q (assume $r_q = 0$)	Hydrogen source: r_m (assume $r_m = 0$)

3.1 Implementation in UMATHT subroutine

Subroutine UMATHT is usually used to define the thermal constitutive behaviour of the material and internal heat generation during heat transfer processes. In this paper a UMATHT is used to implement the hydrogen diffusion equation. The quantities that are defined in a UMATHT are summarized in Table 2. It is essential to note that the variation of internal energy with temperature

and with spatial temperature gradient i.e. $\frac{\partial U_q}{\partial T};\ \frac{\partial U_q}{\partial\left(\frac{\partial T}{\partial x}\right)}$ respectively in the heat procedure

correspond to the variation of chemical potential with hydrogen concentration at NILS C_L and with trap density gradient function of plastic strain ε_P in equation (1.10) i.e. $\frac{\partial U_m}{\partial C_L};\ \frac{\partial U_m}{\partial\left(\frac{\partial N_T}{\partial \varepsilon_P}\right)}$

respectively. Moreover the variation of heat flux with temperature and with spatial temperature gradient i.e. $\frac{\partial \vec{J}_q}{\partial T};\ \frac{\partial \vec{J}_q}{\partial\left(\frac{\partial T}{\partial x}\right)}$ respectively corresponds to the variation of internal energy with

hydrogen concentration at NILS C_L and with the hydrogen concentration gradient i.e. $\frac{\partial \vec{J}_m}{\partial C_L};\ \frac{\partial \vec{J}_m}{\partial\left(\nabla C_L\right)}$. The hydrogen diffusion equations can be written using the formalism appropriate for the subroutine as follows:

$$\rho U_m\left(t+\Delta t\right)=\rho U_m\left(t\right)+\frac{\partial \rho U_m}{\partial C_L}dC_L+\frac{\partial \rho U_m}{\partial N_T}\frac{dN_T}{d\varepsilon_p}d\varepsilon_p+\frac{\partial \vec{J}_m}{\partial C_L}dC_L-\frac{\partial \vec{J}_m}{\partial \nabla C_L}d\nabla C_L \tag{1.14}$$

The terms of equation (1.14) can be obtained by manipulation equations (1.9-1.12) as follows:

$$\begin{aligned}
&\frac{\partial \rho U_m}{\partial C_L}=D_{eff}=1+\frac{N_T K_T N_L}{\left(K_T C_L+N_L\right)^2}\\
&\frac{\partial \rho U_m}{\partial N_T}=\frac{K_T C_L}{K_T C_L+N_L}\\
&\frac{\partial \vec{J}_m}{\partial C_L}=\frac{DV_H}{RT}\vec{\nabla}\sigma_H\\
&\frac{\partial \vec{J}_m}{\partial\left(\nabla C_L\right)}=-DI
\end{aligned} \tag{1.15}$$

Where *I* is the identity matrix.

It is essential to note the in order to calculate the gradient of hydrostatic stress $\vec{\nabla}\sigma_H$ in equation (1.13) we need to use a USDFLD subroutine. USDFLD allows as defining field variables at a material point as functions of time or of any of the available material point quantities in this case the direct components of stress: σ_{11}, σ_{22}, σ_{33}. USDFLD calls the utility routine i.e. GETVRM to provide access to the values of the material point quantities at the start of the increment. In order to evaluate the gradient of hydrostatic stress we interpolate the hydrostatic stress inside the element at each gauss point. The interpolation is identical to the procedure used to calculate the displacement field from the nodes of the element. We use a common block to store the nodal values, which enables the gradient to be calculated without needing to resort to a UEL. However 4 – node coupled temperature-displacement plane strain elements CPE4T cannot be used for this purpose because the strain operator implemented in Abaqus for linear plane strain elements provides constant volumetric strain throughout the element, therefore the gradient of hydrostatic stress within the element is zero. Although linear plane stress elements could be used we prefer to use plane strain elements as the UMAT can more readily be extended to 3D using a plane strain formulation. Therefore we use quadratic 8 – node coupled temperature-displacement plane strain elements CPE8T.

Table 2. Quantities that need to be coded in the UMATHT.

HEAT EQUATION	MASS DIFFUSION EQUATION
Quantity to be defined in the UMATHT	Quantity to be defined in the UMATHT
$\frac{\partial U_q}{\partial T};\ \frac{\partial U_q}{\partial\left(\frac{\partial T}{\partial x}\right)},\ \frac{\partial \vec{J}_q}{\partial T};\ \frac{\partial \vec{J}_q}{\partial\left(\frac{\partial T}{\partial x}\right)}$	$\frac{\partial U_m}{\partial C_L};\ \frac{\partial U_m}{\partial\left(\frac{\partial N_T}{\partial \varepsilon_P}\right)},\ \frac{\partial \vec{J}_m}{\partial C_L};\ \frac{\partial \vec{J}_m}{\partial\left(\nabla C_L\right)}$

4. Numerical results

The example in Figure 2 illustrates a plate with the hole subjected to a displacement field and hydrogen concentration $\overline{C}=1$ at the edge of the hole. $\overline{C}$ is the hydrogen concentration in the lattice calculated as number of hydrogen atoms per unit volume normalized with respect to the maximum number of interstitial hydrogen atoms. $\overline{C}$ varies between 0 and 1. $\overline{C}=1$ means that all the interstitial sites are occupied by hydrogen atoms. We consider a quarter of the plate with symmetric boundary conditions as shown in figure 2. We also impose no-flux on the bottom side. A description of the effect of the hydrogen content on the flow stress in the matrix is given as follows [1-3]:

$$\sigma_Y = \sigma_0^H \left(1 + \frac{\varepsilon_P}{\varepsilon_0}\right)^{\frac{1}{n}} \tag{1.16}$$

Where $\sigma_0^H = \Psi(C_L)\sigma_0$ is the initial yield strength in the presence of hydrogen that decreases with increasing hydrogen concentration. $\Psi(C_L)$ is a monotonically decreasing function of hydrogen concentration at NILS. ε_0 is the initial yield strain in the absence of hydrogen, ε_P is the plastic strain and n is the hardening exponent which is considered not to be affected by hydrogen. For simplicity, we will ignore swelling due to introduction of hydrogen into a material. Equation (1.16) has been implemented in a UMAT subroutine within ABAQUS (ref). Equation (1.16) models the effect of hydrogen-induced material softening, this is to be viewed as an attempt to describe the experimental observations of the effect of hydrogen on dislocation mobility (Sofronis, 1989; Robertson, 1999; Robertson, 1986). Figure 3 shows the distribution of the concentration of hydrogen in the plate. Hydrogen is localized in the area where the hydrostatic stress is high such at the edge of the hole. Figure 4 illustrates how the initial yield strength is affected by the presence of hydrogen $\sigma_0^H = \Psi(C_L)\sigma_0$. In the regions where the hydrogen content is high (i.e. at the edge of the hole) the value of the flow stress is considerably reduced by 20% .The presence of hydrogen promotes softening of the material and localization of plastic flow (HELP). Figure 5 show the distribution of plastic strain that is localized in the area where (a) the concentration of stress in higher and (b) hydrogen concentration reach its maximum value.

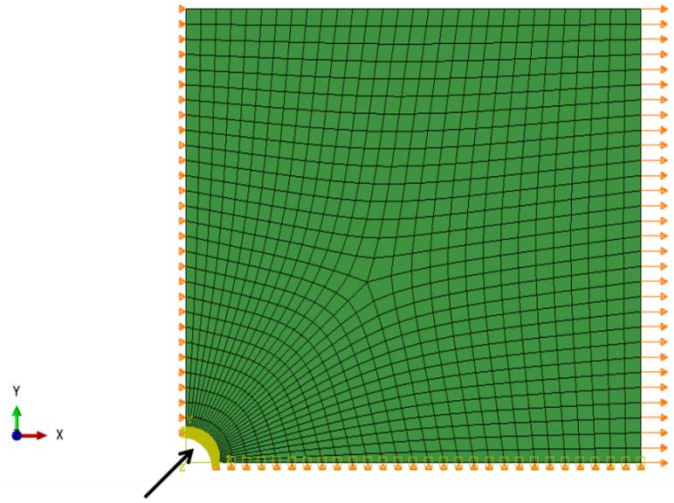

Figure 2. Plate with the hole subjected to a displacement field and hydrogen concentration at the edge of the hole

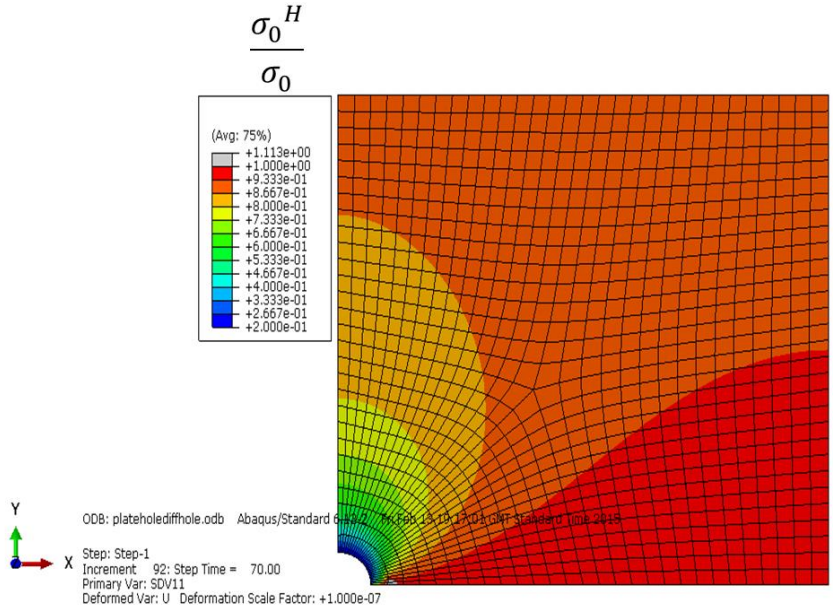

Figure 3. Distribution of the concentration of hydrogen inside the plate, max concentration of hydrogen is localized at the edge of the hole.

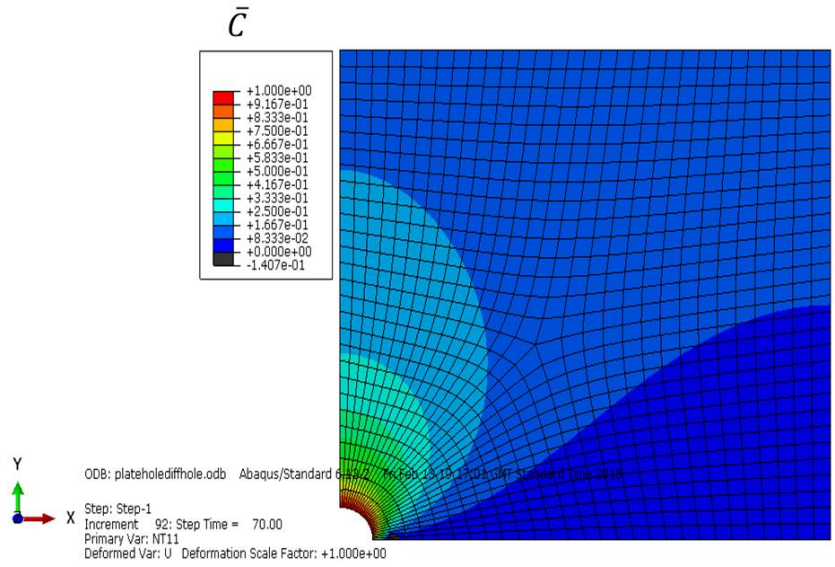

Figure 4. Distribution of the function $\Psi\left(C_L\right)=\frac{\sigma_0^H}{\sigma_0}$ inside the plate.

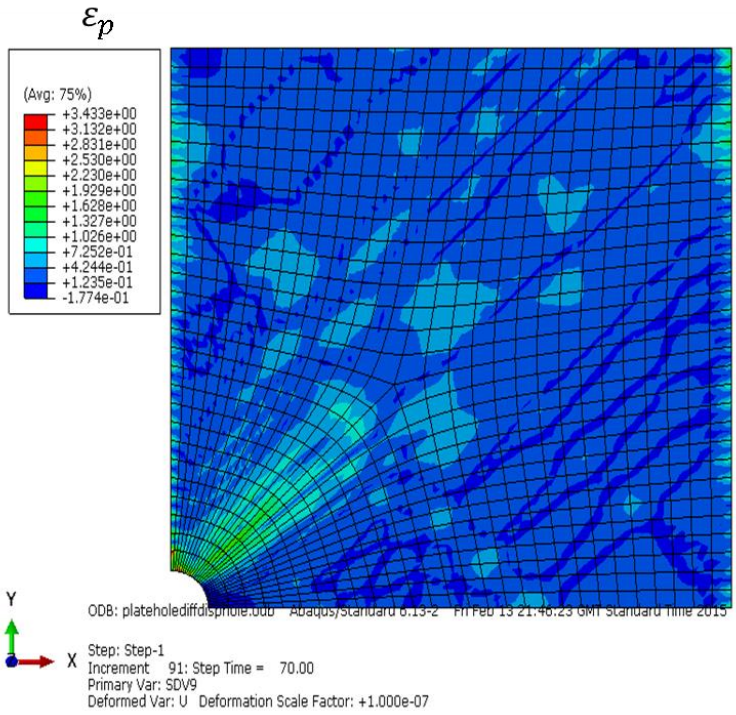

Figure 5. Distribution of plastic strain inside the plate.

5. Conclusions

This paper deals with coupling hydrogen diffusion equation with the plastic response of high strength steel. We show a strategy in order to implement the hydrogen diffusion equation in a UMATH in which we also calculate the component of the gradient of hydrostatic stress needed to solve the hydrogen diffusion equation. This model can be used to study the HELP (Hydrogen Enhanced Local Plasticity) mechanism.

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