Two-dimensional numerical modelling of hydrogen diffusion assisted by stress and strain

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Abstract

This work is based on previous research on the one-dimensional (1D) analysis of the hydrogen diffusion process, and proposes a numerical approach to simulate the phenomenon in two-dimensional (2D) situations, e.g., near notches. The *weighted residual method* was used to solve numerically the differential equations set out when the geometry was discretized through the application of the *finite element* technique. This developed procedure can be a suitable practical tool to analyze hydrogen embrittlement phenomena in structural materials.

Keywords: numerical modelling, weighted residual method, hydrogen diffusion, axisymmetric notch.

1 Introduction

The influence of hydrogen on fracture depends on hydrogen concentration, C, in the sites where localized material damage might occur. The accumulation of hydrogen in these zones proceeds by diffusion from external or internal sources, i.e., local fracture event takes place when and where hydrogen concentration reaches some critical value, C_{cr}, which is conditioned by the stress-strain state in material [1]. This is expressed by the following equation

$$C_{cr} = C_{cr}(\sigma_i, \varepsilon_i) \tag{1}$$

that reflects the influence, in a general case, of the stress-strain state through its invariants, represented by the principal components of stresses and strains σ_i and ε_i (i = 1, 2, 3), respectively.

Hydrogen diffusion within metals is also known to be governed by the stress-strain state therein. Roughly, it may be considered that hydrogen diffuses in metals obeying a Fick type diffusion law including additional terms to account for the effect of the stress-strain state. Concerning the role of stress, this is

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commonly associated with its hydrostatic component σ. According to this, hydrogen diffuses not only to the points of minimum concentration (driven by its gradient), but also to the sites of maximum hydrostatic stress (driven by its gradient). The diffusion process may be also conditioned by the plastic strain.

Following this way, i.e., considering the *diffusion assisted by stress and strain* as a responsible transport mode, it is possible to evaluate the amount of hydrogen accumulated in metal, and this way to determine the locations where fracture initiation process might take place in hydrogen embrittlement phenomena.

In order to improve the understanding of the diffusion phenomena inside materials, and particularly the effects that stresses exert on diffusion, it is useful to reveal the time evolution of hydrogen concentration in the relevant sites concerning particular geometries of the studied test-pieces or components, especially in the more representative locations therein.

To this end, numerous analyses have focused on various aspects of hydrogen diffusion in metals affected by mechanical factors, such as stress or strain. Some analytical closed-form solutions as well as numerical approaches have been developed under certain more or less restraining assumptions or simplifications. Concerning these latter, several previous studies were limited to considerations with one spatial dimension of the sole diffusion depth and straight-line diffusion flux (1D situations), but with an advantage of taking explicitly into account a lot of complicating factors which could arise during nonsteady-state elastoplastic loading histories. Several analyses dealt with two-dimensional (2D) situations, when diffusion was disturbed by geometrical or stress-state inhomogeneities and proceeded along curvilinear trajectories, e.g. near notches or cracks. However, these studies have been notably less extensive so far, in particular as regards the nonsteady-state stress-strain fields, e.g., slow strain-rate test conditions or cyclic loading. Thus the present paper aims to give a preliminary depiction of some advances towards the modelling of 2D stress-strain assisted hydrogen diffusion under transient loading conditions.

2 Problem statement

To save the space, further development deals solely with stress assisted diffusion since its generalization for the case of stress-assisted diffusion is straightforward. According to previous studies [2], it is assumed that hydrogen diffusion through material proceeds toward the sites where the lowest concentration or the higher hydrostatic stresses occur. The combination of these factors results in an equation for the stress-assisted diffusion flux of hydrogen which is:

$$\vec{J} = -D\,\nabla C + D\,\Omega\,C\,\nabla\sigma \quad \text{with} \quad \Omega = \frac{V_H}{RT} \tag{2}$$

where D is the hydrogen diffusion coefficient, V_H is the partial molar volume of hydrogen in metal, R the universal gas constant and T the absolute temperature.

Following the standard way, using the *matter conservation law* [3]:

$$\frac{dC}{dt} = -\mathrm{div}\vec{J} \tag{3}$$

together with the expression (2) for the flux, the equation of diffusion in terms of the sole concentration can be obtained

$$\frac{dC}{dt} = \nabla(D\,\nabla C - D\,\Omega\,C\,\nabla\sigma) \tag{4}$$

In this formulation, neither stress state, nor temperature (and thus, temperature dependent material characteristics, such as D or Ω) are required to be stationary, but can be time dependent. To simplify this preliminary study, diffusion coefficient, D, as well as temperature is considered to be spatially uniform, i.e., their gradients are zero, although this is not an essential restriction. This leads to the equation of stress-assisted hydrogen diffusion in terms of concentration:

$$\frac{dC}{dt} = D\,(\nabla^2 C - \Omega\,\nabla C\,\nabla\sigma - \Omega\,C\,\nabla^2\sigma) \tag{5}$$

where the coefficients may be time dependent.

The geometry of interest, selected here as an example to develop the analysis methodology, is sketched in fig. 1, which shows how the three-dimensional testpiece geometry can be analyzed as a two-dimensional region (shaded figure) due to its axial symmetry.

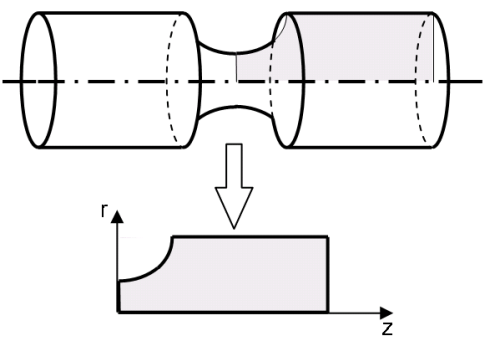

Figure 1: Diagram of analyzed geometry.

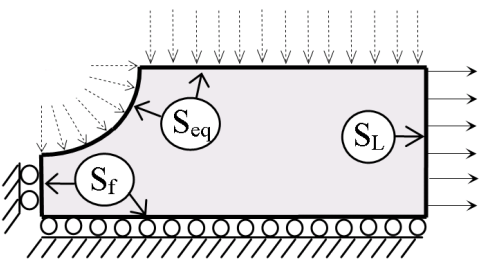

Figure 2: Boundary conditions applied to an axisymmetric geometry.

The boundary conditions, both the mechanical and those for hydrogen entry into metal, are depicted in fig. 2. There an arbitrary axial load is applied over the boundary S_L, a definite environmentally controlled equilibrium concentration of hydrogen, C_{eq}, is imposed over the boundary S_{eq} exposed to the hydrogenating environment, and on both symmetry axes denoted S_f, the null values of the hydrogen flux, $\vec{J}$, and of the normal component of displacement are imposed.

The following expressions represent explicitly the mentioned boundary conditions for diffusion:

$$\vec{J}\cdot\vec{n}\,\big|_{S_f} = J_\Gamma\big|_{S_f} = 0 \tag{6}$$

$$C\,\big|_{S_{eq}} = C_{eq} \tag{7}$$

where $\vec{n}$ is the external unit normal vector to the respective surface. For convenience in further numerical implementation of the diffusion boundary-value problem (5)-(7), the equilibrium equation (7) at the side of hydrogen entry from the environment is substituted by the next mass-exchange condition

$$\vec{J}\cdot\vec{n}\,\big|_{S_{eq}} = J_\Gamma\big|_{S_{eq}} = \alpha\,(C - C_{eq}) \tag{8}$$

where α is the mass-exchange rate coefficient which controls the velocity of approaching the equilibrium of hydrogen between environment and the entry surface layer S_{eq} of a testpiece. To represent adequately the equilibrium entry condition (7) by means of relation (8), this rate coefficient may be chosen arbitrarily, but large enough to ensure practically instantaneous (with respect to the characteristic time scale for diffusion) attainment of the equilibrium given by equality (7). The adequacy of a choice can be easily confirmed *a posteriory*.

Finally, to finish the diffusion problem statement, hydrogen accumulation in the initially hydrogen-free sample may be considered, so that the zero initial condition

$$C\big|_{t=0} = 0 \tag{9}$$

will be placed throughout a whole testpiece of interest.

3 Numerical approach

Obviously, quantitative modelling of stress-assisted hydrogen diffusion requires the stress field in a testpiece of interest to be known. Even for rather simple cases, such as a notched bar being considered here, neither the exact solutions nor the closed form ones are usually available. Thus, one must count on some sort of the numerical solution of the mechanical portion of the coupled problem of the stress-assisted diffusion. The finite element method (FEM) approach, well-developed for both linear and nonlinear analyses of deformable solid mechanics, is a right choice to perform the stress analysis as a prerequisite for diffusion calculations.

In due course, simulation of diffusion which accompanies mechanical loading of a sample also requires numerical treatment. To this end, expansion of the

FEM approach based on the same framework of the spatial finite elements used in the stress analysis is a natural choice for numerical modelling of diffusion.

Some advanced general purpose finite-element codes, well adapted for stress analysis, in particular, e.g. ABAQUS or MSC.MARC, have certain capabilities to simulate the stress-assisted diffusion, too. Unfortunately, they still are limited in some rather important aspects. As regards ABAQUS, this allows to perform simulations of the stress-assisted diffusion governed by equation (5) "over" the data of an accomplished solution of a geometrically and physically nonlinear stress-strain analysis, i.e., for the stationary stress field at the end of some preliminary loading trajectory, but not for the case of simultaneous transient loading and hydrogenation.

Another one, the MSC.MARC code with certain user subroutines may be employed to simulate the transient stress-assisted diffusion as far as corresponding transport equation (5) has mathematically the same form as the equation of convective heat transfer implemented in this software, although, not for the geometrically nonlinear (large deformation) cases. Besides, it has another rather strong shortcoming in that it requires one to define the values of stress gradient at the finite element nodes, which is accompanied by the accuracy loss in the displacement-based FEM procedures. Indeed, there the stresses *per se* are derived with an inevitable loss of accuracy from the displacement gradients, so that the best approximation of stresses is achieved at the element integration points, and calculation of the second derivatives of displacements must worsen the analysis accuracy substantially.

With this in mind, it seems to be a reasonable compromise to consider a FEM implementation of the modelling of stress-assisted diffusion over the previously (or simultaneously) performed stress analysis taking the nodal values of stresses, obtained with a post-processing technique, as the entry data for diffusion, i.e., constructing a finite-element approximation of the stress field with the aid of the same finite-element shape functions used in the mechanical analysis to approximate the displacement fields.

Following this way, the standard weighted residuals procedure together with finite element approximation of both fields of the hydrostatic stress σ and the hydrogen concentration C [6] may be adopted to develop corresponding procedure for diffusion modelling coupled with the stress analysis.

Proceeding with the standard weighted residuals approach [6] to find an approximated solution of the diffusion boundary-value problem (2)-(6) and (8), the approximation of concentration is represented in terms of a linear combination of the spatial trial functions generated over a certain sort of finite elements which discretise the solid under consideration, $N_i(\mathbf{x})$, where $\mathbf{x}$ stands for the instantaneous coordinates of material points over the volume of considered region V occupied by a testpiece, so that

$$C(\mathbf{x},t) = \Sigma\, C_i(t)N_i(\mathbf{x}),\ i = 1, 2, \ldots, n \qquad (10)$$

where C_i is the nodal values of concentration, and the sum is taken over all the nodes of the finite element discretisation. Then, the best approximation of the considered boundary-value problem will be obtained with the nodal concentrations C_i which nullify all the residuals, which correspond to both the

differential equation (5) and the boundary conditions (6) and (8), with the weights $W_i(\mathbf{x})$, so that this yields the system of equations as follows

$$-\int_V W_i \dot{C}\, dV - \int_V \nabla W_i \bullet \left[D \nabla C - D\,\Omega\, C \nabla\sigma\right] dV - \int_{S_f+S_{eq}} W_i \left[\bar{J}_\Gamma - \bar{J}\right] = 0$$

$$\forall\ i = 1, 2, \ldots, n \tag{11}$$

where $\bullet$ represents the inner product.

Adopting the Galerkin method as a particular form of weighted residuals, i.e., considering the weights W_i to be the same as the trial functions N_i, after standard transformations of integrals in the relation (11), the next system of the ordinary differential equations with respect to nodal concentrations $C_i(t)$ may be derived:

$$\sum_j \left\{ \dot{C}_j \int_V N_i\, N_j\, dV + C_j \int_V \left[D\left(\nabla N_j \bullet \nabla N_i\right) - D\,\Omega\,\nabla\sigma\ N_j \bullet \nabla N_i\right] dV \right.$$
$$\left. + \int_{S_f} N_i\, J_\Gamma\, dS + \alpha C_j \int_{S_{eq}} N_i\, N_j dS - \alpha\, C_{eq} \int_{S_{eq}} N_i\, dS \right\} = 0 \tag{12}$$

or in the matrix form,

$$\mathbf{M}\,\dot{\mathbf{C}} + \mathbf{K}\,\mathbf{C} = \mathbf{F} \tag{13}$$

where the dot represents time derivative and the boldface layout is used to denote matrices (vectors).

Within the standard framework of development of the finite element procedures, considering the region V subdivided with a set of finite elements V_e, that is $V = \Sigma V_e$, corresponding global matrices which appear in equation (13) are the result of the assembling of respective element matrices defined as follows

$$\mathbf{m}_e = \int_{V_e} N_i\, N_j\, dV \tag{14}$$

$$\mathbf{k}_e = \int_{V_e} \left[D \nabla N_i \bullet \nabla N_j - D\,\Omega\,\nabla\sigma\, N_i \bullet \nabla N_j\right] dV + \alpha \int_{S_{eq}} N_i\, N_j\, dS \tag{15}$$

$$\mathbf{f}_e = -\int_{S_f} N_i\, J_\Gamma\, dS + \alpha\, C_{eq} \int_{S_{eq}} N_i\, dS \tag{16}$$

where trial functions N_i acquire now the meaning of the corresponding element shape functions.

In these equations the stress-field is supposed to be known as a certain finite element approximation with the use of the same trial functions (or element shape functions) of the form similar to the one employed for the concentration (10), i.e.

$$\sigma(\mathbf{x},t) = \Sigma\, \sigma_i(t) N_i(\mathbf{x}), \qquad i = 1, 2, \ldots, n \tag{17}$$

where $\sigma_i(t)$ are the known nodal stress values over a prescribed loading history, which must be obtained on the phase of purely mechanical analysis. This latter may be performed either simultaneously with or previously to the diffusion calculations, as far as hydrogen diffusion is not supposed to affect the stress-strain state evolution in a solid. Now, having reduced the diffusion boundary-problem to the system of first-order differential equations (12) or (13), the

solution of this latter along the t-axis may be undertaken with the aid of the general easily programmable time-marching numerical scheme proposed for diffusion-type equations elsewhere [7]. Limiting to the first-order approximation of the unknowns within every single time interval, the nodal concentration values $\mathbf{C}_{m-1}$ and $\mathbf{C}_m$ at the start and the end, respectively, of the m-th time interval $[t_{m-1},t_m]$ are related as follows

$$\left(\mathbf{C}_m - \mathbf{C}_{m-1}\right)\left(\mathbf{M} + \theta\,\Delta t\,\mathbf{K}\right)/\Delta t + \mathbf{K}\,\mathbf{C}_{m-1} = \mathbf{F} \tag{18}$$

where $\Delta t = t_m - t_{m-1}$, and the constant θ must be chosen in a manner assuring the stability of this time-marching scheme. Obviously, for the first time interval (at $m = 1$) the array $\mathbf{C}_0$ must be determined according to the prescribed initial conditions of the problem. Then subsequent values of $\mathbf{C}_m$ are to be found from (18) solving corresponding linear algebraic system by any suitable means. In particular, in a symbolic form the matrix equation (18) renders the next solution

$$\mathbf{C}_m = \mathbf{C}_{m-1} + \left(\mathbf{M} + \theta\,\Delta t\,\mathbf{K}\right)^{-1}\left(\mathbf{F} - \mathbf{K}\,\mathbf{C}_{m-1}\right)\Delta t \tag{19}$$

which invites one to employ suitable algorithms of matrix inversion on this route. Described procedure of time integration was proven to be unconditionally stable when $\theta \in [0.5, 1]$.

This way, the numerical approach to the modelling of the stress-assisted diffusion is determined in general terms. Its further transformation into a working practical code follows established FEM procedures of element formulation (i.e., the choice of appropriate element geometry, its shape functions, derivation of respective element matrices, which are involved in equations (13), the use of numerical integration, etc). Since diffusion modelling under consideration is planned as a supplementary one to a stress-strain analysis to be performed with the use of a certain general purpose FEM code, it seems naturally to use the same spatial element formulations for both mechanical and diffusion phases whenever there appeared no specific reasons to change the element type.

Concerning described numerical approach, some final comments are worthy to be made. First, it is known [8] that strong accuracy deterioration may occur when Galerkin method is applied to the transport equation (5), which is a kind of a convection-dominated problem, and a mesh-related parameter called the Peclet number increases too much. In such cases Petrov-Galerkin methods are considered to be a better choice. Fortunately, this complication has never been approached in performed simulations with the magnitudes of governing material parameters associated with common metal-hydrogen systems, considered geometries and loadings, as well as reasonable finite element meshes.

Next, whenever diffusion is considered to proceed simultaneously along with a non-steady state loading history, such as if slow strain rate tests were simulated, the stress-field is obviously time dependent, and so, the stress dependent element matrices do, too. Besides, when large geometry changes occur, the deformed distances become the diffusion paths of interest, so that coordinates $\mathbf{x}$ must be continuously updated with deformation displacements, and thus, they also become time dependent. As a result, all the element matrices in equations (13) must be updated throughout the simulation histories, i.e., they

must be recalculated on every time step of diffusion modelling. This makes the full-scale calculations extremely time consuming. To diminish this, some reasonable model reductions might be not only advisable, but necessary.

4 Improvement of the workability of the developed modelling scheme

To proceed with simulations of stress-assisted diffusion with rather modest computational facilities available, it turned out to be indeed necessary to reduce the FEM-problem size. Among two possible approaches, i.e., coarsening of the mesh of the modelled "full-scale" specimen or shrinking the domain of diffusion simulation focusing on the locations of prospective hydrogen assisted fracture initiation near the notch, the second one seems to be preferable. The relevant data about stress fields may be transferred to this domain from the full scale mechanical analyses, performing their interpolation for the finite element mesh for diffusion, if convenient.

To succeed on this way, in our particular application case of the notched tensile specimens, one may take an advantage of that the notch can act as a localized disturbance of the uniforms stress field in a smooth tensile specimen, depending on notch parameters of depths and width, as it is displayed by the data of the hydrostatic stress distribution in fig. 3.

Figure 3: Hydrostatic stress distribution in a notched bar under traction along the horizontal axis indicating homogenization of the stress-state away from the notch (obtained with the finite element code MSC.MARC).

As well, a notch may do the same with regard to the diffusion from the points of view of the geometry and the stress effects on the transport phenomenon, if compared with the stress-unassisted diffusion in a smooth cylinder. In particular, the range of the disturbing effect of a notch on stress inassisted transport phenomena in solids can be estimated from fig. 4, where vanishing of the notch effect corresponds to fairly radial flow trajectories, or concentration contour bands parallel to the cylinder surface, the same as it occurs in smooth bars.

Thus, it follows that at some reasonable distance from the notch, these effects on hydrogen diffusion (of notch geometry and non-uniform stresses) vanish and diffusion becomes stress-notch unaffected. According to this, a reduced

geometry can be considered, which includes the region of stress-assisted and notch affected transport. This zone of interest may be defined from analyses of the FEM-solutions of the problems of mechanics about the stress-strain state in notched bars and stress-strain unassisted transport, which may be obtained, e.g., with the aid of whichever available FEM-code, such as examples displayed in figs. 3 and 4. To this end it is only necessary to substitute the rest of the specimen (the "remote" portion) by corresponding boundary conditions derived, e.g., from the available closed-form solution of the transport problem for smooth homogeneous cylinder, which may be found elsewhere [9].

As an example, the reduced size domain to calculate the stress affected distribution of diffusible hydrogen in a particular tensile notched specimen, the same as considered above, is verified as shown in fig. 5, where corresponding boundary conditions are indicated. There a mesh of linear triangular elements is employed, although, this is not a matter of particular essence with respect to the presented approach.

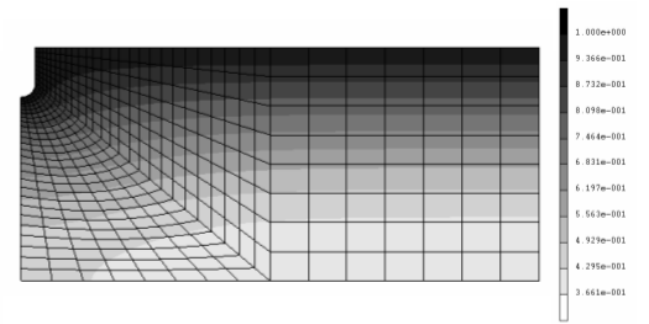

Figure 4: Diffusing specie distribution in a bar in the course of stress-strain-unassisted diffusion.

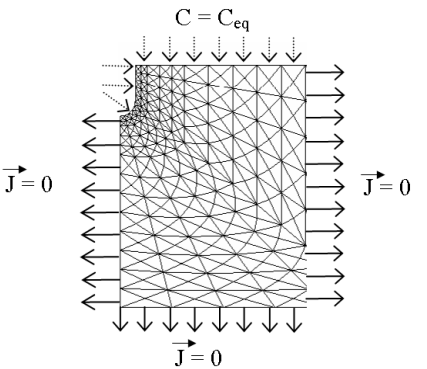

Figure 5: Reduced size domain and boundary conditions for simulations of stress assisted diffusion.

5 Conclusions

The numerical approach presented in this paper allows one to calculate the distribution of hydrogen in stressed solids with limited expenditure of computer resources. Its generalization for the case of stress and strain assisted diffusion is straightforward.

This model is considered to be useful to improve the knowledge of the role played by the factor of hydrogen accumulation in prospective rupture sites by stress-strain assisted diffusion, one of the key items in hydrogen embrittlement, a very dangerous phenomenon that frequently accompanies structural metals and alloys in service.

Proposed computational model seems to be a promising tool as an aid to develop the life-prediction analyses for metallic components and structures subjected to any kind of hydrogen embrittlement in service.

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