EFFECT OF HYDROSTATIC STRESS IN THE VICINITY OF A NOTCH ON HYDROGEN EMBRITTLEMENT

J. Toribio[1] and M. Elices[2]

The relevant role of hydrostatic stress in hydrogen diffusion in pearlitic steel is outlined by performing slow strain rate tests (SSRT) on axisymmetric notched samples at different strain rates under simultaneous hydrogen charging by cathodic polarization. The use of different notch geometries allows a study of the influence of the hydrostatic stress state in the vicinity of the notch tip on hydrogen diffusion. In the quasi-instantaneous tests, the value of hydrostatic stress at the sample boundary (just the notch tip) at the failure instant is relevant from the fracture point of view. Concerning the quasi-static tests, the maximum value of the stress triaxiality in each geometry (ratio of the hydrostatic to the equivalent stress) seems to govern the diffusion process.

INTRODUCTION

When a sample is tested in a corrosive medium with electrochemical techniques, hydrogen embrittlement is a phenomenon associated not only with cathodic potentials, but also with anodic ones, although in the latter case the main damage mechanism is anodic dissolution, as demonstrated by Parkins *et al.* (1). Hydrogen transport phenomena in iron and steel have been studied by many researchers, but the results are sometimes contradictory, and the problem is not yet fully understood, as pointed out by Hirth (2).

The aim of the present paper is to formulate, on the basis of thermodynamic considerations, equations for stress-assisted diffusion of hydrogen in metals, including not only the effect of the concentration differences, but also that of the hydrostatic stress gradient, which conditions the transport, making the hydrogen diffuse towards the regions of maximum hydrostatic stress and modifying the boundary condition for the diffusion partial differential equation. In addition, hydrogen embrittlement tests under different triaxial stress states ahead of the notch allow a study of the role of hydrostatic stress in the transport phenomena.

[1] Department of Engineering, University of La Coruña, E.T.S.I. Caminos, Pol. de Sabón, Parc. 12-14, 15141 Arteixo, La Coruña, Spain.

[2] Department of Materials Science, Polytechnical University of Madrid, E.T.S.I. Caminos, Ciudad Universitaria, 28040 Madrid, Spain.

DIFFUSION EQUATIONS

A thermodynamic formulation of the diffusion problem, is based on the chemical potential μ_H, which has the following expression (Toribio (3)):

$$\mu_H = D^* \left(\ln c - \frac{V^*}{3RT}\, tr\, \bar{\sigma} \right) \qquad (1)$$

where D* is the diffusion coefficient, c the hydrogen concentration, V* the molar partial volume of hydrogen, R the ideal gases constant, T the absolute temperature and $\bar{\sigma}$ the stress tensor. The hydrogen flux density **J** is:

$$\mathbf{J} = -c\, \mathbf{grad}\, \mu_H \qquad (2)$$

which yields:

$$\mathbf{J} = -D^* \left(\mathbf{grad}\, c + \frac{V^*}{3RT}\, c\, \mathbf{grad}\, tr\, \bar{\sigma} \right) \qquad (3)$$

Applying the mass conservation and the Gauss's Theorem, the following partial differential equation is obtained:

$$\frac{\partial c}{\partial t} = D^* \left[\Delta c - \frac{V^*}{3RT} \left(\mathbf{grad}\, c \bullet \mathbf{grad}\, tr\, \bar{\sigma} + c\, \Delta\, tr\, \bar{\sigma} \right) \right] \qquad (4)$$

where Δ is the laplacian operator. For a free metal boundary in contact with the hydrogen, the boundary condition is:

$$\mu_H = \mu_H^0 \qquad (5)$$

that is:

$$\ln c - \frac{V^*}{3RT}\, tr\, \bar{\sigma} = \ln c_0 \qquad (6)$$

or:

$$c = c_0 \exp \left(\frac{V^*}{3RT}\, tr\, \bar{\sigma} \right) \qquad (7)$$

In the quasi-instantaneous tests (fast enough to assume that there is no hydrogen diffusion towards the inner points), the hydrogen concentration at the boundary is a direct function of the hydrostatic stress ($\sigma = tr\, \bar{\sigma}/3$) at that point:

$$c_\Gamma = c_0 \exp \left(\frac{V^* \sigma_\Gamma}{RT} \right) \qquad (8)$$

In the quasi-static tests (slow enough to neglect time effects) the situation approaches the stationary one, and the concentration at all points of the sample is a direct function of the hydrostatic stress at those points:

$$c(x) = c_0 \exp \left(\frac{V^* \sigma(x)}{RT} \right) \qquad (9)$$

EXPERIMENTAL PROGRAMME

To analyze the role of hydrostatic stress in hydrogen diffusion in pearlitic steel, slow strain rate tests (SSRT) were performed on round notched samples in an aqueous medium which promoted hydrogen embrittlement. Tests were performed on round notched samples with the four notch geometries sketched in Fig.1 (a wide range of notch depths and radii), to achieve different hydrostatic stress distributions in the vicinity of the notch and so influence the hydrogen diffusion.

The material was a hot rolled pearlitic steel supplied in bar form of 12mm diameter. Mechanical properties appear in Table 1. The test environment was an aqueous solution of 1 g/l calcium hydroxide plus 0.1 g/l sodium chloride (pH=12.5). To promote hydrogen embrittlement, all tests were performed with potentiostatic control at constant potential of -1200 mV SCE. A broad range of displacement rates was covered in the SSRT to evaluate different degrees of hydrogen damage. Two limit situations are particullary interesting: the quasi-static test (slow enough to reach stationary conditions for the hydrogen diffusion) and the quasi-instantaneous test (fast enough to avoid hydrogen penetration into the sample). Two fracture tests were performed in air for each geometry, to measure the reference value for the fracture load in absence of environmental attack.

Macroscopic test results showed the typical trend of hydrogen embrittlement tests when plotted against remote strain rate: Fracture load in hydrogen environment increases as the applied strain rate increases, which suggests a behaviour influenced by hydrogen diffusion. For very low values of the strain rate (quasi-static tests), the failure load reaches an asymptotic value corresponding to maximum embrittlement. When the strain rate is below this value, the damage produced by the hydrogen embrittlement does not depend on the strain rate, but on the stress state in the vicinity of the notch tip, and therefore on the geometry. For very high values of the strain rate (ultra-fast tests), the failure load also reaches a limit value corresponding to minimum embrittlement.

ROLE OF HYDROSTATIC STRESS

To study the influence of hydrostatic stress on the hydrogen embrittlement process, elastic-plastic finite element computations were performed with the four geometries used in the experimental programme. One approach would consist in analyzing the role of hydrostatic stress at the boundary sample in the failure load of quasi-instantaneous tests. Since diffusion cannot take place in these tests due to their short duration, the value of σ at the boundary would be relevant, because it influences the hydrogen concentration according to equation (8). Fig. 2 presents the failure load in hydrogen environment (divided by the failure load in air) for the quasi-instantaneous tests of each geometry, as a function of the boundary hydrostatic stress (in dimensionless exponential form) computed at the fracture instant. There is a direct decreasing relationship between the failure load in the quasi-instantaneous tests and the boundary hydrostatic stress at the fracture instant, which allows a quantification of the influence of such a stress on hydrogen ingress, through the boundary concentration.

Another approach is to study the influence of maximum hydrostatic stress on diffusivity, which seems to be relevant in the quasi-static tests. However, this variable does change as the load applied on the sample increases during the test, making difficult a simple numerical approach. It would be useful to consider a parameter related to the maximum hydrostatic stress but remaining constant during the test. In this conceptual frame, the stress triaxiality (ratio of the hydrostatic to the equivalent stress) seems to be adequate, since it is almost constant during the tests (Toribio *et al.* (4)). A triaxiality factor T can be defined as the maximum value of the stress triaxiality in the sample:

$$T = \sup_{\Omega} (\sigma/\bar{\sigma}) \tag{10}$$

where σ is the hydrostatic stress , $\bar{\sigma}$ the equivalent stress (in the Von Mises sense) and Ω the domain. The T-values for geometries A, B, C and D were 0.9, 1.4, 0.5 and 0.4, respectively. Fig. 3 offers the failure load in the quasi-static tests versus the triaxiality factor of each geometry. It is possible to observe a monotonic decreasing dependence, which emphasises the role of maximum hydrostatic stress in hydrogen diffusion.

CONCLUSIONS

1. The hydrostatic stress plays a relevant role in accelerating the diffusion of hydrogen in the sample, both increasing the boundary concentration and enhancing the hydrogen flux associated with stress gradients.

2. The hydrostatic stress at the boundary controls the fracture in the quasi-instantaneous tests, fast enough to avoid hydrogen penetration towards the inner points. In this case the environmental effect is restricted to the notch tip.

3. The triaxiality factor (maximum triaxiality in the sample) governs the fracture in the quasi-static tests, slow enough to allow the stationary solution of the diffusion problem to be reached. In this case the environmental effect depends on the hydrogen diffusion towards the maximum hydrostatic stress points.

ACKNOWLEDGEMENTS

This work was supported by the Spanish Office for Science and Technological Research (CICYT) under Grant MAT91-0113-CE. Acknowledgement is gratefully given to to Mr. J. Monar (Nueva Montaña Quijano Company, Santander, Spain) for providing the steel used in the experimental programme, and to the *Colegio de Ingenieros de Caminos, Canales y Puertos-Demarcación de Galicia,* Spain, for the financial support of technical trips during the final stages of this work

REFERENCES

(1) Parkins, R.N., Elices, M., Sánchez-Gálvez, V. and Caballero, L.. Corros. Sci., Vol. 22, 1982, p. 379.
(2) Hirth, J.P., Metall. Trans. A, Vol. 11A , 1980, p. 861.
(3) Toribio, J., Ph. D. Thesis, Polytechnical University of Madrid, 1987.
(4) Toribio, J., Lancha, A.M. and Elices, M., Mater. Sci. Engng. A, Vol. A145, 1991, p. 167.
(5) Toribio, J. and Elices, M., Corros. Sci. (In press).

TABLE 1 – Mechanical properties of the steel

E (GPa)	σ_Y (MPa)	UTS (MPa)	Ramberg-Osgood $\varepsilon = \sigma/E + (\sigma/P)^n$ P (MPa)	 n
199	600	1151	2100	4.9

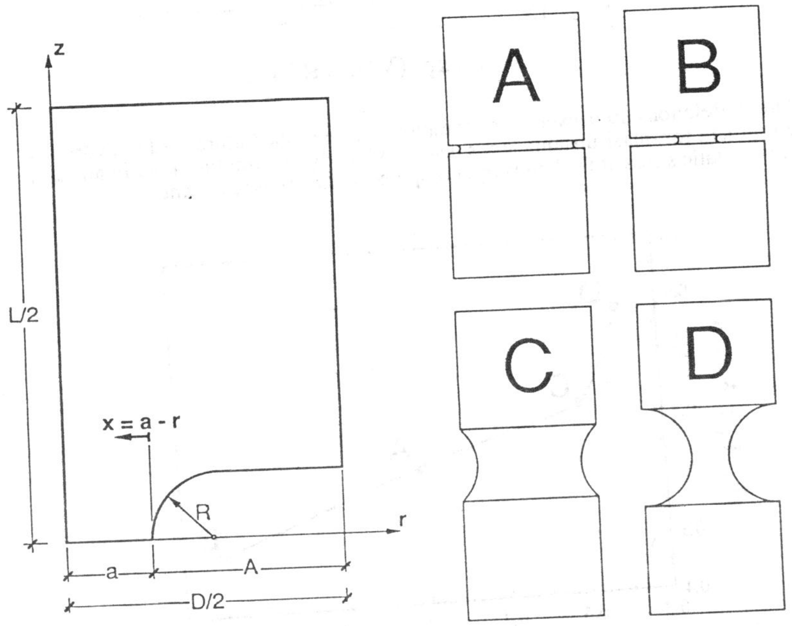

Figure 1. Geometries of the samples (Geometry *A* : R/D = 0.03, A/D = 0.10; Geometry *B* : R/D = 0.05, A/D = 0.39; Geometry *C* : R/D = 0.36, A/D = 0.10; Geometry *D* : R/D = 0.40, A/D = 0.39, where R is the notch radius, A the notch depth and D the sample diameter).

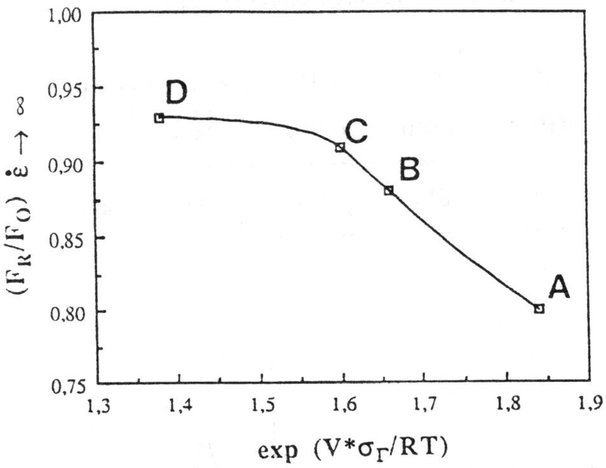

Figure 2. Relationship between the asymptotic value of the failure load in hydrogen environment for quasi-instantaneous tests (divided by the fracture load in air) and the hydrostatic stress at the boundary, computed at the fracture instant.

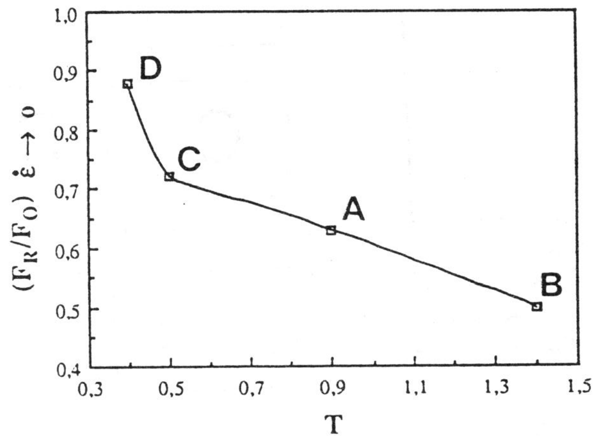

Figure 3. Relationship between the asymptotic value of the failure load in hydrogen environment for quasi-static tests (divided by the fracture load in air) and the triaxiality factor (maximum value of the triaxiality in the sample).