ROLE OF DIFFUSION IN THE HYDROGEN TRANSPORT IN METALS

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In this paper a set of non-conventional hydrogen diffusion equations is proposed. In such equations the flux density of hydrogen depends on both the concentration gradient and the hydrostatic stress gradient.

Fracture tests on notched samples under hydrogen environment obtained by cathodic polarization were performed. The microstructural analysis of the fracture surfaces by scanning electron microscope fractography showed a specific topography in the hydrogen affected region: Tearing Topography Surface (T.T.S.), which can be considered as a damaged zone.

The T.T.S. depth has no relation with the plastic zone size. In the quasi-static tests, the T.T.S. size is equal to the depth at which the hydrostatic stress reaches a maximum value. This fact demonstrates that diffusion is the main transport mechanism of hydrogen in metals.

INTRODUCTION

Hydrogen embrittlement, with loss of ductility and decrease of fracture resistance, plays an important role in stress corrosion cracking, that is, in all fracture processes of metals under aggressive environments. Actually, when a sample is tested in a corrosive medium with electrochemical techniques, hydrogen embrittlement is a phenomenum associated not only with cathodic potentials, but also with anodic ones, although in the latter case the main damage mechanism is anodic dissolution (1).

Clarifying the main mechanism of hydrogen transport in metals is, therefore, a very important topic in Fracture Mechanics under aggressive environments. A great research effort has been made in recent years in this area. The problem, however, is not yet fully understood, and two main types of hydrogen transport in metals are proposed:

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- Hydrogen diffusion (2,3), according to Fick's Laws, which can be modified to take account of physical variables such as temperature, density of hydrogen traps, sulphur content, etc. On the other hand, the theoretical bases of Fick's Laws can be improved, introducing the dependence of hydrogen flux on the hydrostatic stress field in the sample.

- Hydrogen transport by dislocations movement (4), closely associated with plastic deformation. It is possible to model this transport by considering an effective diffusion coefficient dependent on dislocations density, which is a function of equivalent plastic strain.

DIFFUSION EQUATIONS

A thermodynamic formulation of the diffusion problem, based on a Gibbs function, is proposed in this section. In the case of small strains and low hydrogen concentrations the linear theory represents a first approach, and the Gibbs function takes the form (5):

$$G = -\frac{\alpha}{2}\,(\mathrm{tr}\,\boldsymbol{\sigma})^2 - \frac{\beta}{2}\,\boldsymbol{\sigma} \bullet \boldsymbol{\sigma} - \gamma c\;\mathrm{tr}\,\boldsymbol{\sigma} + f(c) \qquad (1)$$

where α, β and γ are constants, c represents the hydrogen concentration and $\boldsymbol{\sigma}$ is the stress tensor; f(c) represents any function of the concentration. On assuming that f(c) takes the form of an integral of a logarithm, the classical Fick's Laws of Diffusion can be obtained. The expression for G is then:

$$G = -\frac{\alpha}{2}\,(\mathrm{tr}\,\boldsymbol{\sigma})^2 - \frac{\beta}{2}\,\boldsymbol{\sigma} \bullet \boldsymbol{\sigma} - \gamma c\;\mathrm{tr}\,\boldsymbol{\sigma} + k \int \ln c \; dc \qquad (2)$$

in which k is a new constant.

The chemical potential of hydrogen can be obtained by deriving the Gibbs function:

$$\mu_H = \frac{\partial G}{\partial c} = k \ln c - \gamma\,\mathrm{tr}\,\boldsymbol{\sigma} \qquad (3)$$

The relative velocity between the hydrogen and the metal yields from the chemical potential:

$$\mathbf{v} = -\,m\,\mathbf{grad}\,\mu_H \qquad (4)$$

where m is a constant and v the relative velocity. From this equation, the hydrogen flux density **J** is:

$$\mathbf{J} = -\, mc\, \mathbf{grad}\, \mu_H \qquad (5)$$

By substituting the expression of μ_H given in (3), a modification of Fick's First Law is obtained, which takes into account that the stress field in the metal affects the hydrogen flux density:

$$\mathbf{J} = -\, km\, \mathbf{grad}\, c + \gamma\, mc\, \mathbf{grad}\, (\mathrm{tr}\, \boldsymbol{\sigma}) \qquad (6)$$

where the term dependent on the stress tensor trace and thus on the hydrostatic stress σ is significant:

$$\sigma = \mathrm{tr}\, \boldsymbol{\sigma} / 3 \qquad (7)$$

Applying the conservation of mass to a volume V limited by a surface S invariable with the time, gives

$$\frac{\partial}{\partial t} \int_V c\, dV = - \int_S \mathbf{J} \cdot d\mathbf{S} \qquad (8)$$

Following Gauss's Theorem, the continuity equation is obtained:

$$\frac{\partial c}{\partial t} = -\, \mathrm{div}\, \mathbf{J} \qquad (9)$$

Substituting the expression of **J** given in (6), a partial differential equation is obtained, which is a modification of Fick's Second Law:

$$\frac{\partial c}{\partial t} = km\, \Delta c - \gamma m\, \mathbf{grad}\, c \cdot \mathbf{grad}\, (\mathrm{tr}\, \boldsymbol{\sigma}) - \gamma\, mc\, \Delta\, (\mathrm{tr}\, \boldsymbol{\sigma}) \qquad (10)$$

If the material is linear and elastic, the latter term $\Delta(\mathrm{tr}\, \boldsymbol{\sigma})$ becomes zero, from the constitutive and compatibility equations:

$$\boldsymbol{\sigma} = \lambda\, (\mathrm{tr}\, \boldsymbol{\varepsilon})\, \mathbf{1} + 2\mu \boldsymbol{\varepsilon} \qquad (11)$$

$$\boldsymbol{\varepsilon} = (\mathbf{grad}\, \mathbf{u} + \mathbf{grad}^{T}\, \mathbf{u}) / 2 \qquad (12)$$

where $\boldsymbol{\varepsilon}$ is the strain tensor, **1** the unity tensor, **u** the displacement vector, and λ and μ the Lamé Coefficients.

The most common boundary condition for the differential equation (10) is that of free metal boundary in contact with the hydrogen, and this is given in terms of chemical potential:

$$\mu_H = \mu_H{}^o \qquad (13)$$

or, in other terms:

$$k \ln c - \gamma \, \mathrm{tr}\, \boldsymbol{\sigma} = k \ln c_o \qquad (14)$$

where c_o is the concentration for hydrogen-metal equilibrium, when the latter is free of stress. Thus:

$$c = c_o \exp\left(\frac{\gamma}{k} \mathrm{tr}\, \boldsymbol{\sigma}\right) \qquad (15)$$

equation which represents both the boundary condition for the diffusion problem and the stationary solution of the problem.

The of elastic strains in the metal can be calculated through derivation of the Gibbs function (2):

$$\boldsymbol{\varepsilon}^e = -\frac{\partial G}{\partial \boldsymbol{\sigma}} = \alpha \, (\mathrm{tr}\, \boldsymbol{\sigma}) \, \mathbf{1} + \beta \boldsymbol{\sigma} + \gamma c \mathbf{1} \qquad (16)$$

And the increment of the strain tensor due only to the hydrogen is:

$$(\Delta \boldsymbol{\varepsilon}^e)_c = \gamma \, (\Delta c) \, \mathbf{1} \qquad (17)$$

The equation (15) can be expanded in Taylor's series:

$$c = c_o \left[1 + \frac{\gamma}{k} \mathrm{tr}\, \boldsymbol{\sigma} + \frac{1}{2} \left(\frac{\gamma}{k} \mathrm{tr}\, \boldsymbol{\sigma}\right)^2 + \ldots \right] \qquad (18)$$

and considering only the first two terms:

$$\Delta c = \frac{\gamma}{k} \, \Delta \, (\mathrm{tr}\, \boldsymbol{\sigma}) \qquad (19)$$

and substituting in (17) yields:

$$(\Delta \boldsymbol{\varepsilon}^e)c = \frac{\gamma^2}{k} \, \Delta \, (\mathrm{tr}\, \boldsymbol{\sigma}) \, \mathbf{1} \qquad (20)$$

increment of elastic strain due to the hydrogen, a term which modifies the constitutive equation of the metal. This term is negligible when the hydrogen concentrations are small. In this case the stress-strain relationship is the one corresponding to innert environment.

Modified Fick's Laws (6) and (10) can be written with the usual symbols:

$$\mathbf{J} = - D^* \operatorname{grad} c + Mc \operatorname{grad} \sigma \tag{21}$$

$$\frac{\partial c}{\partial t} = D^* \Delta c - M \operatorname{grad} c \bullet \operatorname{grad} \sigma - Mc\, \Delta\sigma \tag{22}$$

where σ is the hydrostatic stress ($\sigma = \mathrm{tr}\, \boldsymbol{\sigma}$ (3)), D^* the hydrogen diffusion coeficient and M a second coefficient, function of the first:

$$M = \frac{D^* V^*}{RT} \tag{23}$$

where V^* is the molar partial volume of hydrogen, R the ideal gases constant and T the absolute temperature.

The relationships between the constants k, γ and m used in the present formulation and the common diffusion coeficients are the following:

$$km = D^*$$
$$3\gamma m = M$$
$$3\gamma / k = V^* / RT$$

The boundary condition (15) yields:

$$c = c_o \exp\left(\frac{V^* \sigma}{RT}\right) \tag{24}$$

Boltzmann's distribution where c_o is the equilibrium concentration without stress. This equation is also the stationary solution of the diffusion problem. The stationary hydrogen concentration is a function only of the hydrostatic stress. In the quasi-static tests (slow enough to neglect time effects) the situation approaches the stationary one.

EXPERIMENTAL PROCEDURE

A commercial eutectoid pearlitic steel, supplied in bar form of 12 mm diameter, was used for the experimental programme (E=199 GPa, σ_{02}=600 MPa, σ_u=1151 MPa). The test environment was an aqueous solution of 1 g/l calcium hydroxide plus 0.1 g/l sodium chloride. The pH value was 12.5 and the testing was performed at room temperature. To promote hydrogen embrittlement all tests were performed at -1200 mV SCE. This potential was set by means of an electronic potentiostat and a three electrode assembly, as described elsewhere (5).

Tests were performed on round notched samples with the four notch geometries sketched in Fig.1. The dimensions of the samples were:

Sample	R/D	A/D
A	0.03	0.10
B	0.05	0.39
C	0.36	0.10
D	0.40	0.39

where R is the notch radius, A the notch depth and D the diameter of the sample.

Based on previous experience (1), a range of remote displacement between 5.10^{-9} m/s and 2.10^{-6} m/s was used.

Fractographic analysis of the samples by means of scanning electron microscope technique showed that fracture phenomenum always initiates at an edge region at the notch tip where fracture surface may be classified as TTS (Tearing Topography Surface), according to Thompson and Chesnutt (6), and Costa and Thompson (7). Fig.2 shows an electronic photograph of such a fracture surface, which looks like a micro-damaged region inside the hydrogen affected zone. The scale of the micro-damage is probably below 1 μm, clearly lower than the primitive austenitic grain size of the material. Outside the TTS region, fracture surfaces may be classified as quasi-cleavage (symbol C in Fig. 2).

ANALYSIS OF RESULTS AND CONCLUSIONS

Elastic-plastic finite element computations were carried out with the four geometries used in the experimental programme (5). Two interesting results, useful for determining the main hydrogen transport mechanism were obtained:

- The point of maximum hydrostatic stress - very important in hydrogen diffusion according to equation (24) - is a characteristic geometric datum: it does not depend on the load applied on the sample, but remains constant along the loading process. In samples A and C this point is located next to the notch tip (surface of the sample). For geometries B and D it is just in the center of the sample.

- The plastification spreads over a extended region around the notch, reaching the whole net section of the sample, even for initial states of loading.

On the other hand, the experimental results allow the following conclusions to be drawn:

- In Figs. 3 and 4 the depth of TTS zone (x_{TTS}) vs. the duration of the test (time to rupture of the sample, t_c, exposed in hours) is plotted. A horizontal line corresponding to the value x_s (depth of the maximum hydrostatic stress point) is also represented for each geometry. The depth of the TTS region increases when the duration of the test increases, that is when the displacement rate decreases (there being a longer period for hydrogen to diffuse).

- The asymptotic value of x_{TTS} for quasi-static tests coincides with x_s, the depth of the maximum hydrostatic stress point, that is:

$$\lim_{t_c \to \infty} x_{TTS} = \lim_{\dot{\varepsilon} \to 0} x_{TTS} = x_s \, ; \qquad x_s = x_s \text{ (geometry)} \qquad (25)$$

- The limit value of x_{TTS} of x_{TTS} for very fast tests is not zero. This fact demonstrates that the embrittlement effect of hydrogen is not negligible, even for very short durations of the test. It is possible to write:

$$\lim_{t_c \to 0} x_{TTS} = \lim_{\dot{\varepsilon} \to \infty} x_{TTS} = x_o \, ; \qquad x_o = x_o \text{ (geometry)} \qquad (26)$$

where $\dot{\varepsilon}$ represents the strain rate in the test.

- In all geometries there is absolutely no relationship between the size of hydrogen affected region (TTS) and the plastic zone size.

- The afore-mentioned considerations confirm that diffusion is the main transport mechanism of hydrogen in metals for this kind of steel (pearlitic, high strength steels) and in cathodic polarization environmental conditions. The TTS region is thus the zone damaged by the hydrogen, and its depth is influenced by the hydrostatic stress distribution in the sample, which governs the diffusion phenomenum according to the modified Fick's Laws proposed in this paper.

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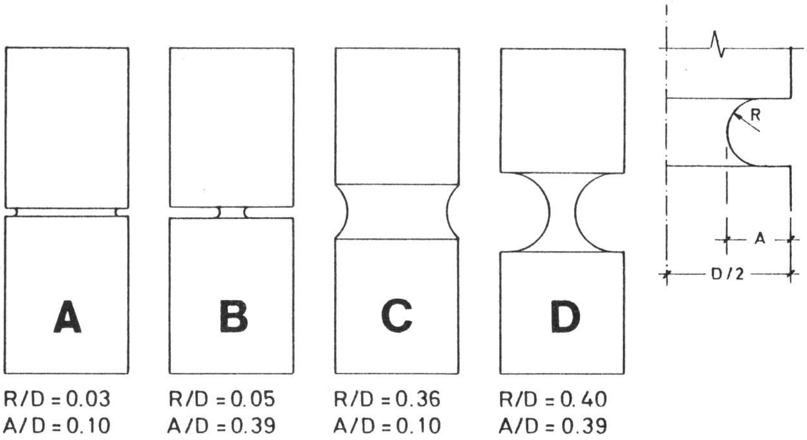

Figure 1. Geometries of the samples

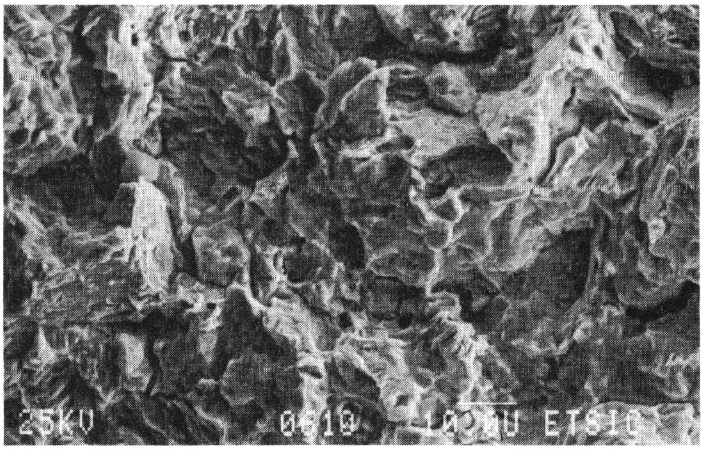

Figure 2. Tearing Topography Surface

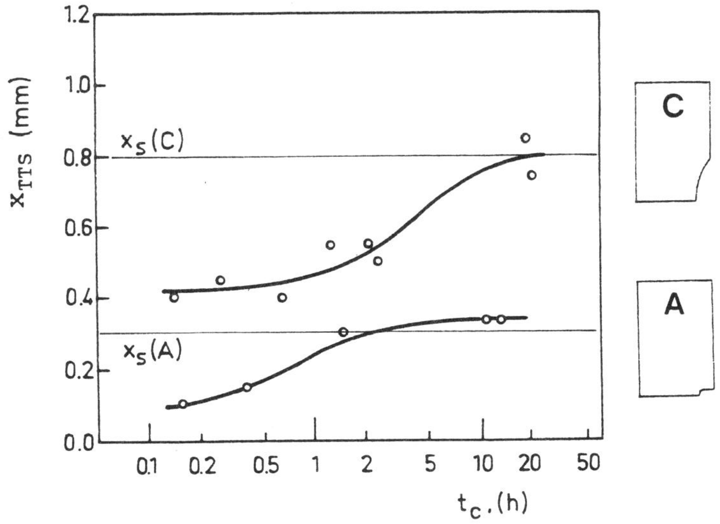

Figure 3. Depth of TTS zone vs. time to rupture (A and C)

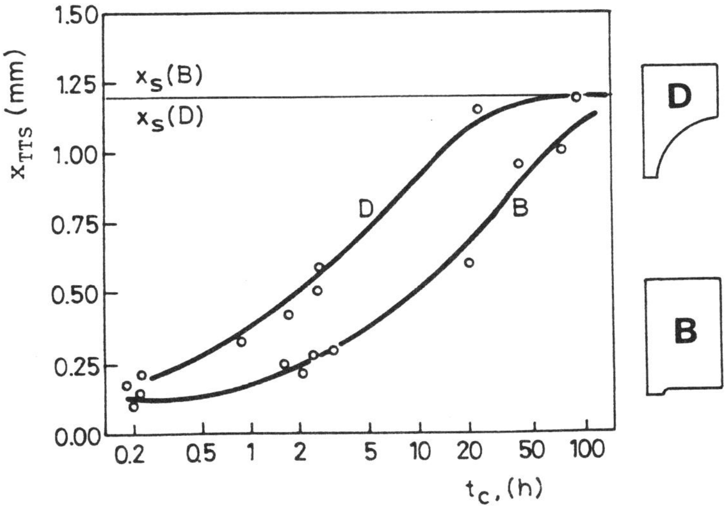

Figure 4. Depth of TTS zone vs. time to rupture (B and D)