

Hydrogen-plasticity interactions in pearlitic steel: a fractographic and numerical study

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Received 27 March 1996; revised 31 May 1996

Abstract

A fractographic and numerical approach is presented to analyze hydrogen-plasticity interactions in pearlitic steel and to elucidate the main hydrogen transport mechanism in this material under triaxial stress states produced by notches. Fractographic analysis showed that the microdamage produced by the hydrogen was clearly detectable by scanning electron microscopy (SEM), through a specific microscopic topography associated with hydrogen effects (tearing topography surface or TTS). Numerical computations obtained by using an elastic-plastic finite element program gave the progressive spreading of the plastic zone, closely associated with the movement of dislocations. In the majority of cases, the plastic zone (PZ) clearly exceeds the hydrogen affected region (TTS) and has no relation with it. In some tests, however, the hydrogen-induced micro-damage surpasses the only region in which there is dislocation movement, and in this case the net macroscopic transport of hydrogen cannot be attributed to dislocation dragging, but only to a random-walk stress-assisted diffusion. Therefore, in spite of the fact that dislocational transport of hydrogen has been sufficiently demonstrated on a microscopic scale, it might not be a hydrogen embrittlement mechanism per se, detectable with loss of fracture load, on a macroscopic scale.

Keywords: Hydrogen-plasticity interactions; Hydrogen embrittlement; Hydrogen affected region; Tearing topography surface (TTS); Pearlitic steel

1. Introduction

Hydrogen embrittlement of metals and alloys is a general phenomenon of degradation of mechanical properties which involves hydrogen transport to the prospective fracture locations, and there seems to be general agreement that hydrogen transport plays a dominant role in hydrogen assisted fracture. The question of the main hydrogen transport mechanism being operative over long penetration distances is still open, and two basic transport modes have been proposed to explain the phenomenon: *diffusion* [1–3] (also called lattice diffusion, random-walk diffusion or $\sqrt{Dt}$ diffusion) and *dislocation sweeping* [4–6] (or dislocation dragging). A key point is to determine whether the main part of *macroscopic* hydrogen transport, that resulting in embrittlement with *detectable* loss of mechanical properties, is carried out by random-walk lattice diffusion or by dislocation movement, the latter associated with interactions between hydrogen and plasticity.

Diffusion is a transport mode by which hydrogen moves towards the points of minimum concentration through the crystalline lattice in the form of random-walk governed by the $\sqrt{Dt}$ term which controls the penetration distance [1]. If stress-assisted diffusion is considered [2], hydrogen movement is driven by the gradients of both concentration and hydrostatic stress. In the case of a formulation on the basis of stress- and strain-assisted diffusion [3], the plastic strain magnitude should be considered as one of the governing factors of hydrogen diffusion. A mechanism of hydrogen transport based on lattice diffusion is consistent with the results of slow strain rate tests under cathodic polarization environmental conditions, since it predicts maximum embrittlement at the slowest strain rates. On the other hand, diffusion is usually a slow transport mode and penetration distances are rather small.

Dislocation sweeping is a transport mode by which hydrogen is dragged by dislocations as the plastic zone spreads. This process may be associated with the average velocity of dislocations which can be macroscopically expressed in terms of the plastic strain rate. There

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are two main models to evaluate the possible supersaturation or enrichment of hydrogen at specific sites in the material as a result of a dislocation sweep-in of hydrogen: the *stripping model* by Tien et al. [4] and the *annihilation model* by Johnson and Hirth [5], both reviewed in [6]. The first estimates a significant build-up of hydrogen, while the latter concludes that the kinetic supersaturations are extremely small in all real situations. The weakest point of the two models is their inconsistency with the well known experimental evidence of the inverse dependence of hydrogen embrittlement upon strain rate (over a certain range of strain rates). The stripping model predicts maximum hydrogen embrittlement at an intermediate strain rate, whereas according to the annihilation model the kinetic supersaturation is proportional to the strain rate.

The two transport modes, diffusional and dislocational, are essentially different. The first one is operative under both sustained and transient (time-dependent) stress-strain states, has hydrostatic stress and *instantaneous* plastic strain as responsible variables, and evolves towards equilibrium hydrogen distributions. In contrast, the other one proceeds exclusively during continuing (dynamic) straining, has plastic strain *rate* as the governing variable, and results in non-equilibrium hydrogen distributions (temporal localised over-saturations). They are fed by newly arriving dislocations which drive hydrogen into specific microstructural sites, from which hydrogen escapes by diffusion to restore thermodynamic equilibrium with local surroundings. Quickly after the end of straining, those hydrogen over-saturations completely relax to local equilibrium by *short-range* (local) diffusion. The efficiency of this mode of hydrogen transport results from competition between these two effects.

Thus the role of hydrogen transport by dislocation dragging is strongly linked with hydrogen-plasticity interactions in the steel. The relationship between hydrogen and plasticity is a fundamental topic which has been the object of many controversial discussions in two opposite senses: whether or not hydrogen influences plasticity development by promoting slip bands or strain localization, and conversely, whether or not plastic zone development, and subsequent movement of dislocations, can affect hydrogen transport. Thus, a key question arises: whether or not dislocation transport can be considered an embrittlement mechanism per se with *detectable* loss of mechanical properties as a consequence of macroscopic hydrogen transport.

Louthan [7], using a linear irreversible thermodynamic argument, suggested that the concept of symmetry of the Onsager coefficients could be applied to hydrogen transport by mobile dislocations, thereby considering the coupled problem of hydrogen-dislocations interactions [$H \leftrightarrow \perp$] in the double sense: (i) hydrogen transport by dislocations or dislocational

transport of hydrogen [$\perp \rightarrow H$]; (ii) dislocation transport by hydrogen or hydrogen-enhanced strain localization [$H \rightarrow \perp$]. Therefore, since dislocations are able to carry hydrogen, the presence of hydrogen is able to promote dislocation movement in the form of slip band and strain localization. From the macroscopical point of view, it seems plausible that to the extent that hydrogen does not affect the macroscopic constitutive equation of the metal, the transport of hydrogen by dislocation sweeping should not have a macroscopic effect.

There is clear evidence of interactions between hydrogen and dislocations in iron single crystals. Hwang and Bernstein have demonstrated dislocation transport of hydrogen [$\perp \rightarrow H$] in single crystal iron [8,9] and, conversely, hydrogen-induced dislocation movement [$H \rightarrow \perp$] and subsequent slip band localization [10], although it is said that at high strain rates a certain percentage of the dislocations exceed the break-away velocity above which the hydrogen can no longer keep up with the moving dislocations. The effect of hydrogen on the behaviour of dislocations [$H \rightarrow \perp$] in iron has been directly observed by Tabata and Birnbaum [11] by in situ deformation techniques in the environmental cell of a high voltage electron microscope.

Experimental support of hydrogen transport by movement of dislocations in metals is given by Donovan's tests of sorption and release of tritium in nickel, iron, stainless steel and aluminium [12,13]. Sorption experiments [12] showed that plastic deformation in a tritium atmosphere not only produced greater tritium sorption, but also decreased the apparent diffusivity as a consequence of enhanced trapping [13]. Release tests evidenced hydrogen-dislocation interactions with an increase in the release rate caused by plastic deformation.

Kurkela and Latanision [14] performed hydrogen permeation experiments in nickel, and Kurkela et al. [15] in fully bainitic steels. In plastically deformed nickel [14], the 'effective' or 'apparent' diffusivity was found to be five orders of magnitude greater than the corresponding value for unstrained nickel, which seems to demonstrate that dislocation transport of hydrogen is the predominant mechanism in deformed nickel, whereas lattice diffusion is probably the predominant one in unstrained nickel. In addition, the observed transport rates agree with the predictions of the stripping model of dislocational transport proposed by Tien et al. [4]. These results are clearly in contrast to the behaviour observed by the same authors (and co-workers) in fully bainitic steels [15] in which hydrogen permeation experiments undergoing simultaneous hydrogen charging and plastic deformation indicated that dislocations act as traps for hydrogen and decrease the rate of hydrogen transport.

The stripping model of dislocation sweeping has been applied to the modelling of hydrogen-assisted subcriti-

cal crack growth [16] and fatigue crack growth [17]. The hydrogen penetration distances due to random walk lattice diffusion and dislocation sweep-in are compared in papers [14,17,18], concluding that the former is considerably smaller than the latter. The calculations are based on the assumption of the validity of single Fick's laws for lattice diffusion. Nevertheless, penetration distances would be much higher considering stress-assisted hydrogen diffusion, since in this case the hydrostatic stress at the boundary increases the hydrogen absorption, and hydrostatic stress gradients accelerate the diffusion of hydrogen (although diffusivity itself can be considered as independent of stress). By the same reasoning, the experimentally observed requirement of *simultaneous* mechanical loading and hydrogen charging to detect measurable macroscopic hydrogen embrittlement has been frequently attributed [19] to the necessity of plastic deformation while hydrogen charging proceeds. However, it is unclear whether the unavoidable requirement is the presence of plastic strain or hydrostatic stress *or both*, since in a real hydrogen embrittlement test under rising load these two macroscopic variables progress, and frequently it is difficult to separate their effects.

On the other hand, there are also several research works in which the dislocational mode of hydrogen dragging is questioned as a mechanism of accelerating hydrogen transport or producing macroscopic embrittlement, in spite of its well established foundations as a microscopic mechanism of transport on the basis of hydrogen-plasticity interactions. As a matter of fact, Zakroczyński [20] observed no accelerating effects of plastic deformation on hydrogen transport in iron, nickel and stainless steels, the evaluation being carried out by hydrogen permeation experiments on samples electrochemically charged with hydrogen. Thus, the experimental results did not support the assumption that moving dislocations accelerate hydrogen transport, since the production of dislocation results in two competing effects: enhanced transport and trapping.

Furthermore, West and Louthan [21] do not question the existence of hydrogen transport by dislocation sweeping (clearly demonstrated), but its role on hydrogen embrittlement. On the basis of hydrogen embrittlement tensile tests on austenitic stainless steels, they suggest that dislocational transport is not required in the embrittlement process, since it can be modelled without the necessity of deformation enhanced hydrogen localization, so other variables such as constraint (triaxiality), hydrostatic tensile stress, local lattice dilation or localized hydrogen content may play a more important (if not decisive) role in hydrogen-assisted fracture. The same authors [22] show that hydrogen absorption raises the yield strength of the

austenite lattice, which indicates that hydrogen inhibits dislocation motion and therefore is not consistent with locally enhanced ductility as a mechanism of hydrogen assisted fracture in austenitic stainless steels, and thus dislocation transport may not play a vital role in hydrogen embrittlement of this kind of steel.

A mixed approach to analysing hydrogen transport during plastic deformation in iron was presented by Hashimoto and Latanision [23] in a model which takes macroscopic diffusion into account in describing dislocation-hydrogen interactions, to include two effects: hydrogen trapping by newly generated dislocations and hydrogen transport by mobile dislocations. The analysis concludes that the increase of flux due to dislocation transport is negligible since it is totally dominated by the strong dynamic trapping effect, although dislocation transport becomes important when lattice hydrogen concentration is small so that most of the hydrogen is trapped in dislocations. The same authors [24] analyze the strain rate dependence of hydrogen embrittlement in terms of hydrogen transport, explaining the phenomenon by the dynamic trapping effect and suggesting that hydrogen trapped in dislocations is responsible for the cracking process.

In addition, experiments of hydrogen embrittlement carried out under torsional (mode III) loading by Green et al. [25] and Swanson et al. [26] resulted in a very slight embrittlement, measured as the ratio of the critical stress intensity factor in hydrogen to the same value in air. The reason may be that in the vicinity of the crack tip hydrostatic tensile stress is minimum, and equivalent stress (in the Von Mises sense) is maximum in these mode III experiments. It seems to indicate that stress-assisted diffusion plays a more important role than dislocation transport, at least from the macroscopic point of view. Previous works on pearlitic steels by Toribio et al. [27] also support this hypothesis of stress-assisted diffusion as the rate-determining step in hydrogen embrittlement, since the size of the zone microscopically affected by the hydrogen was seen to be governed by the hydrostatic stress distribution in the vicinity of the notch tip.

This paper tries to establish experimental bases to clarify the main hydrogen transport mechanism in pearlitic steel, i.e. whether the major amount of hydrogen transport to potential fracture sites in the metal is carried out by random-walk lattice diffusion or by dislocation dragging. The analysis is performed on the basis of fractographic examination of the hydrogen-assisted micro-damaged region in the hydrogen embrittlement tests and by elastic-plastic numerical analysis to obtain the evolution of the plastic zone and to elucidate the role of hydrogen-plasticity interactions in the macroscopic hydrogen embrittlement mechanism.

Table 1
Chemical composition of the steel (wt.%)

C%	Mn%	Si%	P%	S%	Fe%
0.85	0.60	0.26	0.010	0.030	balance

2. Experimental programme

The material used in this research was a hot rolled pearlitic steel supplied from commercial stock by *Nueva Montaña Quijano Company* (Santander, Spain), in bar form of 12 mm diameter. This steel presents a coarse pearlitic microstructure (pearlite interlamellar spacing 0.3 μm). It is the steel used in the production of cold drawn wire for prestressed concrete, after patenting in a molten lead bath to produce fine pearlite (interlamellar spacing around 0.1 μm). Chemical composition and mechanical properties appear in Tables 1 and 2, respectively. The true stress–strain curve of the steel, experimentally measured by means of a tension test, is given in Fig. 1, together with the Ramberg–Osgood modelling used in the numerical analysis.

The specimens were round notched samples of the four geometries sketched in Fig. 2, with the dimensions as shown in Table 3, where R is the notch radius, A the notch depth and D the diameter of the sample ($D = 11.25$ for all specimens, after machining). The use of notched geometries allows a study of the influence of the stress state in the vicinity of the notch tip on hydrogen embrittlement. The stress state near the notch tip influences the hydrogen transport because hydrogen diffusion in the sample is governed not only by the concentration gradient, but also by the hydrostatic stress gradient [2].

Slow strain rate tests were performed with a broad range of displacement rates between 10^{-10} and 2.10^{-6} m s^{-1} , to study the transient (time-dependent) effect of the environment on the metal under different stress triaxiality conditions (different geometries). The test environment was an aqueous solution of 1 g l^{-1} Ca(OH)_2 plus 0.1 g l^{-1} NaCl with pH value of 12.5. The electro-chemical potential was -1200 mV SCE (cathodic), constant for all tests, to promote hydrogen embrittlement. Fig. 3 shows the experimental device and the measuring procedure used in the tests. Samples were coated with insulating lacquer except at the notch surface, to concentrate the environmental attack in the

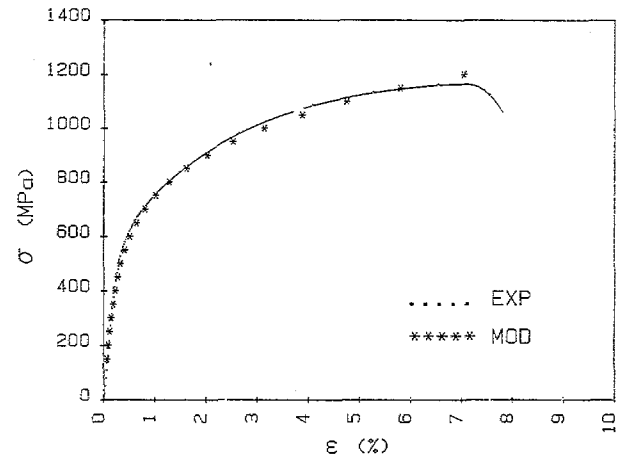


Fig. 1. True stress–strain curve of the steel, experimentally measured by a tension test (...), together with the Ramberg–Osgood modelling used in the numerical analysis (***).

vicinity of the notch. Two fracture tests in air were performed with each geometry, to serve as a reference value for the hydrogen embrittlement test and to check the accuracy of the numerical analysis, as explained in further sections of this paper.

Fig. 4 gives the experimental results of the slow strain rate tests under hydrogen embrittlement environmental conditions, as a plot representing failure load in the solution (divided by failure load in air) versus crosshead speed or testing displacement rate. The critical load in hydrogen increases as the crosshead speed increases or the time to failure decreases, a consequence of the shorter time for hydrogen diffusion. Results also depend on the geometry of the sample, thus demonstrating the influence of the triaxial stress state in the vicinity of the notch tip (very different from one geometry to another).

3. Fractographic analysis: hydrogen affected region

Scanning electron microscopy (SEM) fractographic analysis showed a characteristic region in the vicinity of the notch tip where the microscopic mode of failure is the so called *tearing topography surface* (TTS) [28,29]. The microscopic appearance of such a surface appears in the micrograph of Fig. 5, and it looks like a micro-damaged region inside the hydrogen affected zone. It is possible to say that much of the TTS fracture area

Table 2
Mechanical properties of the steel

Young modulus (GPa)	Yield strength (MPa)	U.T.S. (MPa)	Elongation at UTS (%)	Ramberg-Osgood P(MPa)	$\epsilon = \sigma/E + (\sigma/P)^n$ n
199	600	1151	6.1	2100	4.9

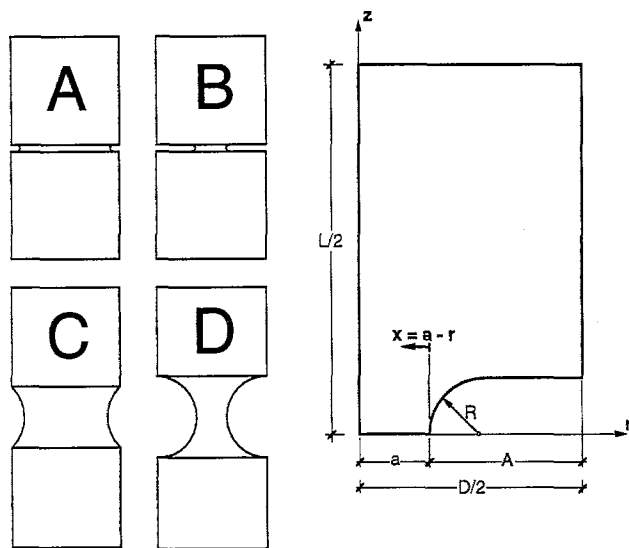


Fig. 2. Notched geometries used in the experimental programme (dimensions in Table 3).

consists of microplastic tearing. Outside the TTS region, final fracture takes place by cleavage in an unstable manner, and clear river patterns can be observed, starting from the TTS region where fracture initiates. The TTS depth was measured in all cases, following the procedure sketched in Fig. 3.

TTS fracture is not due to hydrogen alone, but it also requires stress (or strain effects), and the rupture takes place when a combination of hydrogen and stress (and also strain) levels is reached. However, there is strong evidence which allows the consideration of the TTS zone as the hydrogen-assisted micro-damage region. It is supported by the following experimental facts observed in constant strain tests on pre-cracked specimens and slow strain rate tests on pre-cracked and notched samples:

- The microscopic appearance of the TTS region resembles micro-damage, micro-cracking or micro-tearing due to hydrogen degradation [30]. This experimental finding agrees fairly well with the descriptions reported by Keefe et al. [31] and Nair and Tien [32] about micro-cracking (or micro-damage) produced by the hydrogen.
- The TTS micro-fracture mode is a slow, or subcritical, crack growth topography associated with the

Table 3
Dimensions of the samples (R , notch radius; A , notch depth; D , sample diameter)

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

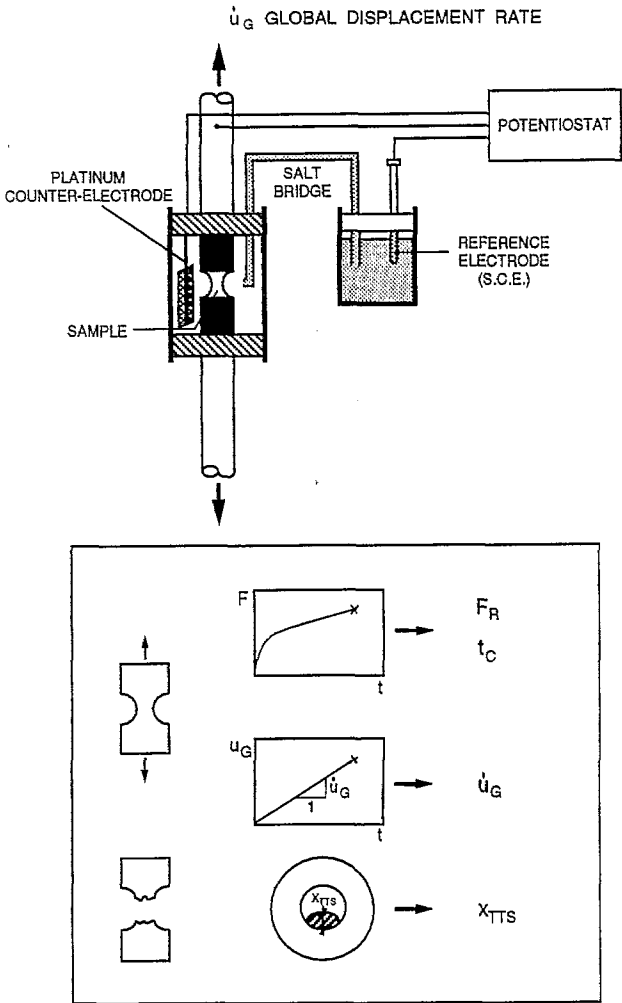


Fig. 3. Device used in the slow strain rate tests under hydrogen embrittlement environmental conditions, and procedure for measuring the test variables.

- stage II or *plateau* in the crack growth kinetics curve, i.e. it corresponds to purely environmental control of crack growth, in this case due to the hydrogen presence in the vicinity of the crack tip [30].
- TTS appears *only* under cathodic potentials (associated with hydrogen environment), but not under anodic ones (associated with anodic dissolution), thereby providing fractographic evidence of hydrogen effects, and replacing the micro-void coalescence (MVC) initiation mode observed in air environment [30].
 - The TTS size increases when the electro-chemical potential becomes more cathodic or negative. This is a consequence of the higher amount of hydrogen at the specimen surface for the more cathodic potentials, which raises the boundary condition for the hydrogen diffusion problem [33].
 - The TTS size slightly increases as the pH decreases (becomes more acid), since the amount of hydrogen

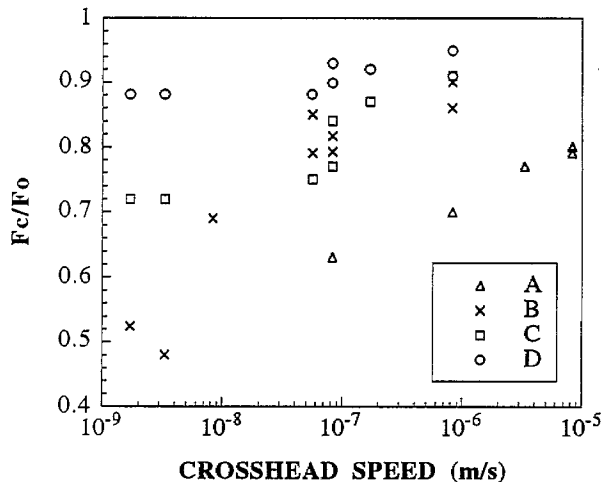


Fig. 4. Experimental results of the hydrogen embrittlement tests: failure load in solution (divided by the same in air) vs. crosshead speed during the test.

supplied to the sample is higher for lower pH values [33]. The effect is really slight as a consequence of the well known local acidification in the vicinity of the crack tip, independently of the bulk pH value [34,35].

- The TTS size clearly decreases as the fatigue load increases. The reason for this is the presence of compressive residual stresses near the crack tip, induced during fatigue precracking. The stronger the fatigue load, the higher the compressive residual stresses, and the less the penetration of hydrogen into the sample [33].
- Experiments conducted at very different strain rates also showed an increasing trend of the TTS size as the time to failure increases (or the externally applied strain rate decreases), a consequence of a mechanism of transport based on stress-assisted hydrogen diffusion and time derivatives [36].

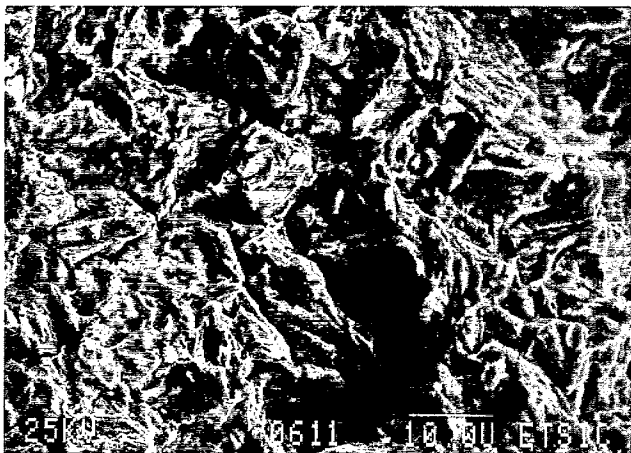


Fig. 5. Microscopic appearance of the hydrogen-assisted micro-damage region.

- The TTS size is clearly influenced by the geometry of the sample, through the hydrostatic stress distribution in its vicinity, which is also consistent with an association between the TTS failure mode and the hydrogen embrittlement process on the basis of a diffusion transport mechanism [36].
- The asymptotic depth of the TTS region for quasi-static tests (slow enough to allow the stationary condition for the hydrogen diffusion problem to be achieved) reaches the point of maximum hydrostatic stress in the sample, which confirms that hydrogen diffuses towards the points of maximum hydrostatic stress [36].

The association between the TTS and the hydrogen-assisted micro-damage process allows an approach to clarify which is the main mechanism of hydrogen transport in pearlitic steels. The TTS size has to be compared with the distribution of hydrostatic stress in the sample, or with the extension of the plastic zone, depending on the mechanism of hydrogen transport under consideration. If lattice diffusion was the predominant mechanism, then the hydrostatic stress would be an outstanding variable. On the other hand, if hydrogen was mainly transported by dislocation sweeping, then the evolution and size of the plastic zone would be relevant, since outside that zone there is no movement of dislocations.

4. Numerical analysis: evolution of the plastic zone

To obtain the progress of the plastic zone as the load on the samples increases, a numerical analysis was carried out on the geometries under study. The finite element method (FEM) with an elastic–plastic code was applied, using a Von Mises yield surface with an incompressible constitutive equation (classical plasticity).

The material model used in the computations corresponds to the real high strength steel used in the experimental programme, whose stress–strain curve, as a relationship between equivalent stress and strain, was introduced into the computer program by means of the following Ramberg–Osgood equation:

$$\varepsilon = \sigma / 19\,9000 + (\sigma / 2100)^{4.9}, \quad \sigma \text{ in MPa} \quad (1)$$

whose graphical representation is plotted in Fig. 1.

The external load was applied step by step, in the form of nodal displacements. An improved Newton–Raphson method was adopted, which modified the tangent stiffness matrix at each step. The finite elements used in the computations were isoparametric with second-order interpolation (eight-node quadrilaterals and six-node triangles).

In Fig. 6 the elastic–plastic FEM computations for all geometries, in the form of load versus displacement

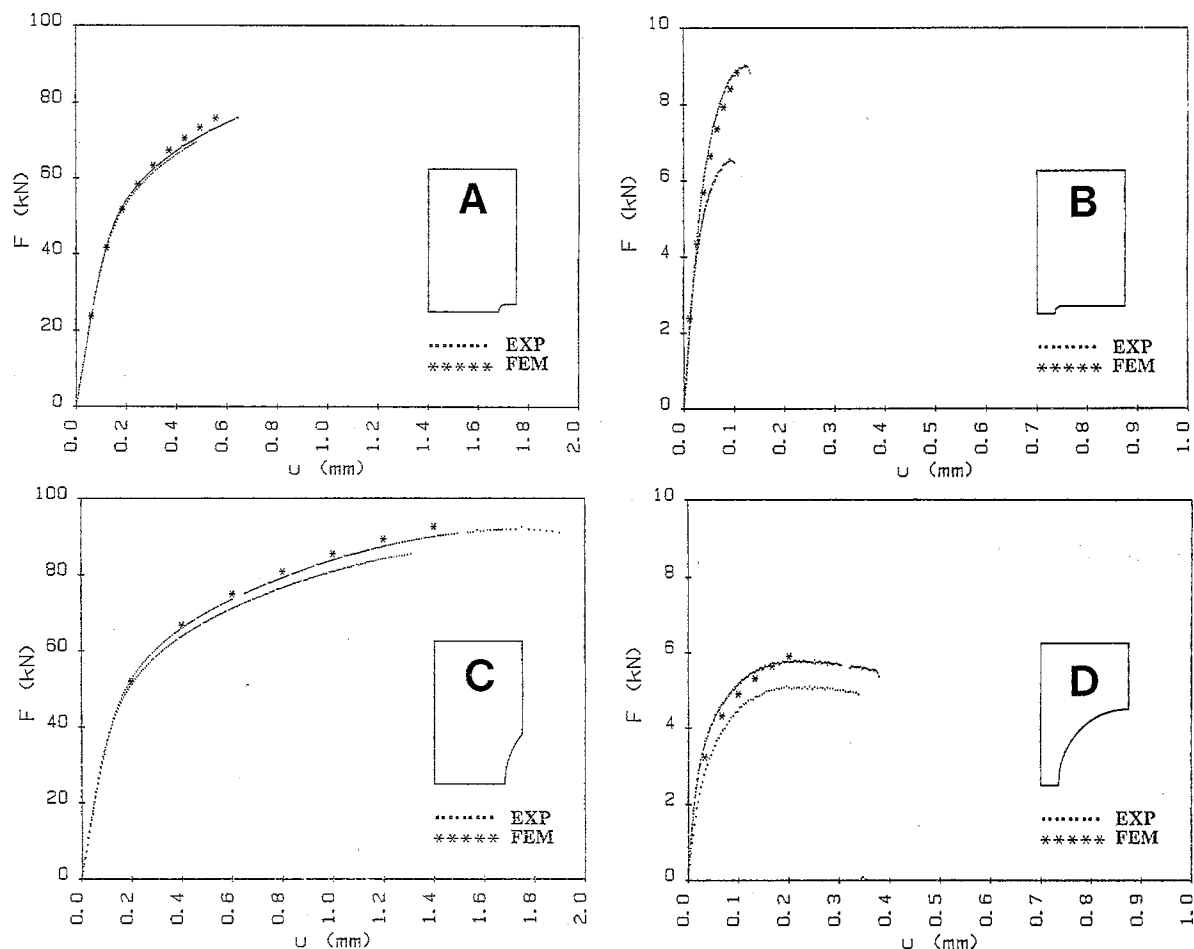


Fig. 6. Experimental results of the two reference fracture tests in air for each geometry (...) in the form of load vs. displacement during the tests, and numerical modelling by the finite element analysis (***)

curve, are compared with the experimental results of the fracture tests in air. The agreement is very good, since the numerical results are always within the experimental scatter band (two fracture tests for each geometry). Therefore, the computer FEM analysis is seen to be adequate to model the evolution of the plastic zone in the samples at any stage of the loading process of the hydrogen embrittlement tests.

The elastic-plastic FEM analysis also demonstrated that the hydrostatic stress levels changed with the loading process, but the point of maximum hydrostatic stress always remains at depth x_s (characteristic of the geometry) from the notch tip, as reported in [27]. Fig. 7 gives typical hydrostatic stress distributions in the samples (only the lines of constant hydrostatic stress are shown, but not the numerical values which obviously increase with the external load applied on the sample). For the geometries B and D the maximum hydrostatic stress point is placed at the centre of the net section (the bar axis) and hydrogen is 'pumped' towards this point by long-term stress-assisted diffusion.

To analyze the evolution of the plastic zone, the yielding criterion used in the numerical computations was that of Von Mises:

$$\bar{\sigma} = \sigma_Y \quad (2)$$

where σ is the effective or equivalent stress and $\sigma_Y = \sigma_{0.1} = 500$ MPa, yield strength measured at 0.1% of strain. Properly speaking, it is the limit of material linear behaviour.

According to this criterion, the boundaries of the progressive plastic zones for different values of the global displacement u_G appear in Fig. 8, where u_G represents the displacement between sample ends (L and D are the length and diameter of the sample, respectively). Curves correspond to different values of the dimensionless parameter u_G/D ($L/D = 4$) and therefore they reflect the progressive spreading of the plastic zone as the external load applied on the sample, external displacement, increases. In all cases, computation was extended up to the situation corresponding to the fracture of the specimen in the test performed in air (see Section 2). Fig. 8 shows that plastic deformation always

initiates at the notch tip and spreads towards the inner part until the whole net section is under plastic regime, this result being general for all the geometries analyzed. Considering the shape of the plastic zone, two considerations may be made:

(i) Geometry A presents a plastic zone which starts from the notch tip and branches as it approaches the sample axis. Its mechanical behaviour is similar to that of a plastic hinge, opening in the vicinity of the notch tip and keeping the rest of the net section stiff.

(ii) The spreading of the plastic zone is global in geometries A and C (plastic zone covers an important part of the sample), whereas it is localized in geometries B and D (plastic zone is restricted to the sample neck).

(iii) With regard to the cross sectional area, the plastic zone spreads broadly in most cases (geometries A, C and D), covering rapidly the whole net section or cross sectional area of the notched geometries. However, in geometry B it develops narrowly in comparison with the other geometries, which indicates that dislocation movement, and its associated hydrogen transport, in this specimen is restricted to a certain region.

Therefore, for the purposes of the present analysis, the main advantage of geometry B is that hydrogen is attracted to the centre of the section, thus producing a broader affected region detectable by fractographic analysis, while at the same time providing a plastic zone small enough to restrict the movement of dislocations to a reduced area. The probability of detecting hydro-

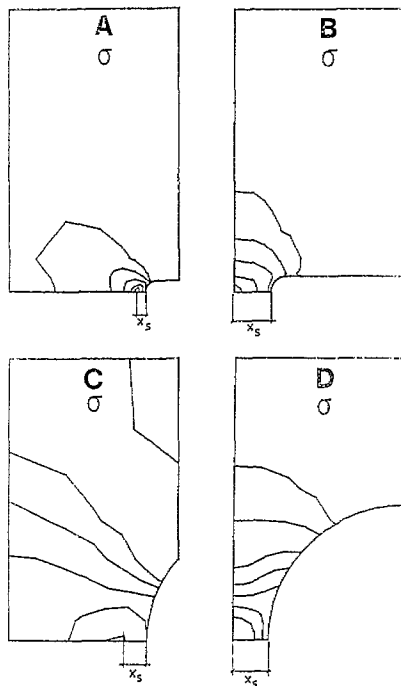


Fig. 7. Hydrostatic stress distribution in the samples (after elastic regime), where x_s is the depth of the maximum hydrostatic stress point towards which hydrogen diffuses.

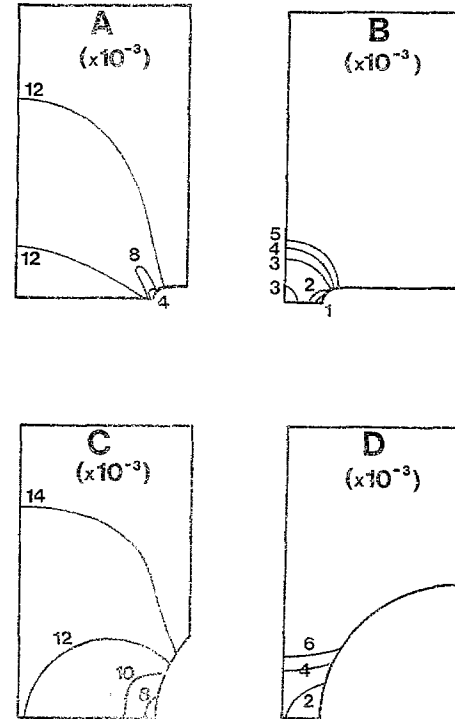


Fig. 8. Spreading of the plastic zone in all geometries, for different values of u_G/D , where u_G is the global displacement applied to the sample reference ends ($L = 4D$) and D the sample diameter.

gen effects outside the plastic zone is high in this sample.

Fig. 9 offers the load-displacement curve for all geometries (numerically computed), together with the plastic zone spreading for different steps of loading (shaded areas), which provides a knowledge of the depth of the plastic zone (in the cross sectional area) for each level of loading, and therefore at the end of the different slow strain rate tests shown in Fig. 4, each test represented by the fracture load in hydrogen which can be introduced into the plots of Fig. 9 (vertical axis) to ascertain the extension of the plastic zone at the end of the test.

5. Discussion

Table 4 gives the comparison between the depth of the hydrogen affected area (TTS) and that of the region with mobile dislocations (PZ) at the end of each hydrogen-embrittlement test. The first was measured by SEM on the hydrogen-assisted micro-damage topography, whereas the latter was numerically computed by an elastic-plastic FEM on the basis of the Von Mises yielding criterion. The table also includes the depth x_s of the maximum hydrostatic stress point, a characteristic of the geometry which can also be numerically computed.

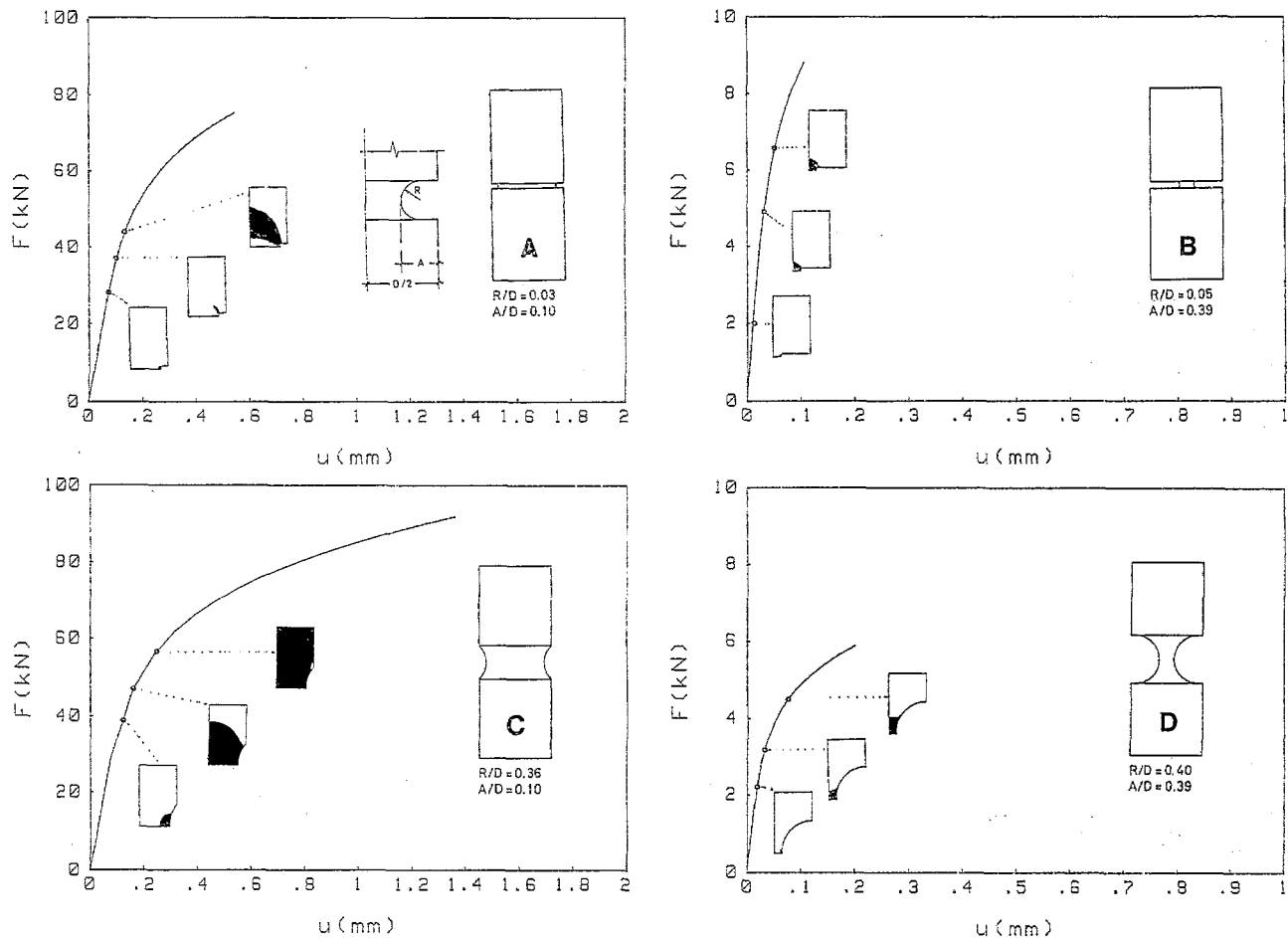


Fig. 9. Load-displacement curves (numerically computed) for each geometry, showing the evolution of the plastic zone (shaded area).

First of all, Table 4 illustrates the afore-mentioned fact that the asymptotic depth of the hydrogen-affected region (TTS) for quasi-static tests, slow enough to allow the stationary hydrogen concentration to be achieved, approaches the depth of the maximum hydrostatic stress point, which in the special geometry B coincides with the sample centre and represents the place towards which hydrogen penetrates if stress-assisted diffusion is considered as a predominant mechanism of transport.

With regard to the relationship between hydrogen and plasticity, it is shown in Table 4 that in the majority of cases the plastic zone (PZ) clearly exceeds the hydrogen affected region (TTS) and has no relation with it. This experimental fact does not prove anything about the hydrogen transport by dislocation sweeping, since the TTS region is completely surrounded by the plastic zone where dislocations move. It only demonstrates that there is no net macroscopic balance of hydrogen transport, detectable by microscopical damage produced by the hydrogen, in the whole extension of the plastic zone.

Nevertheless, for the geometry B ($R/D = 0.05$, $A/D = 0.39$) and for the two slowest tests, the situation is inverse; in this case the hydrogen affected area (TTS) surpasses the plastic zone, i.e. the only region in which there is dislocation movement, and the hydrogen transport cannot be attributed to dislocation dragging, but only to a random-walk lattice diffusion. It is not, however, conventional diffusion according to classical Fick's laws, but stress-assisted diffusion in which the hydrostatic stress field plays a very important role in raising the boundary condition of the diffusion problem and accelerating the diffusion as a consequence of hydrostatic stress gradients, thereby enlarging the penetration distances [36]. For the special geometry B, the maximum hydrostatic stress point is located exactly at the centre of the sample and hydrogen is pumped towards this point.

The same central placement of the maximum hydrostatic stress point is obtained in the elastic-plastic finite element analysis of geometry D, and the asymptotic TTS region also reaches the centre of the specimen. However, in this case the extension of the plastic zone is so large, even in the shortest experiments, that it

Table 4

Depth of the tearing topography surface (TTS) and the plastic zone (PZ) at the end of the hydrogen embrittlement tests (fracture instant)

Geometry	x_S (mm)	x_{TTS} (mm)	x_{PZ} (mm)	$\dot{u}_G$ (m s ⁻¹)	t_c (s)
A	0.30	0.10	SAMPLE AXIS	4.79×10^{-7}	555
		0.10	SAMPLE AXIS	4.81×10^{-7}	570
		0.15	SAMPLE AXIS	1.82×10^{-7}	1365
		0.30	SAMPLE AXIS	3.68×10^{-8}	5370
		0.34	SAMPLE AXIS	3.96×10^{-9}	39 960
		0.34	SAMPLE AXIS	3.26×10^{-9}	48 600
B	1.20	0.10	NET SECTION	1.00×10^{-7}	720
		0.15	NET SECTION	1.03×10^{-7}	780
		0.25	NET SECTION	1.02×10^{-8}	5760
		0.21	NET SECTION	8.70×10^{-9}	7380
		0.27	NET SECTION	6.90×10^{-9}	8520
		0.30	NET SECTION	6.23×10^{-9}	11 160
		0.60	NET SECTION	6.02×10^{-10}	75 600
		0.93	0.33	1.87×10^{-10}	143 040
		1.00	0.41	1.12×10^{-10}	262 800
C	0.80	0.40	NET SECTION	1.83×10^{-6}	516
		0.45	NET SECTION	9.71×10^{-7}	972
		0.40	NET SECTION	3.45×10^{-7}	2295
		0.55	NET SECTION	1.54×10^{-7}	4500
		0.55	NET SECTION	6.67×10^{-8}	7560
		0.50	NET SECTION	5.47×10^{-8}	8340
		0.85	NET SECTION	5.85×10^{-9}	68 400
		0.75	NET SECTION	5.33×10^{-9}	75 000
D	1.20	0.10	NET SECTION	2.13×10^{-7}	660
		0.21	NET SECTION	2.06×10^{-7}	780
		0.33	NET SECTION	4.55×10^{-8}	3240
		0.41	NET SECTION	2.45×10^{-8}	6300
		0.60	NET SECTION	1.49×10^{-8}	9000
		0.50	NET SECTION	1.35×10^{-8}	9420
		1.15	NET SECTION	6.98×10^{-10}	182 400
		1.20	NET SECTION	3.93×10^{-10}	324 000

 x_S depth of the maximum hydrostatic stress point for each geometry; x_{TTS} depth of the TTS region or hydrogen affected area; x_{PZ} depth of the plastic zone at the end of each test; $\dot{u}_G$ global displacement rate; t_c time to failure or critical time.

makes it impossible to separate plasticity from hydrogen induced micro-damage, a general problem difficult to solve in hydrogen assisted fracture under complex stress-strain fields.

The above considerations do not try to refute hydrogen transport by dislocation sweeping, which has been sufficiently demonstrated on a microscopic scale [8–13]. No conclusion can be drawn about this topic; if any, only the difficulty of demonstrating that there is a net transport by dislocation dragging towards a specific site where fracture initiates, so as to permit the consideration of dislocation transport of hydrogen as an embrittlement mechanism per se with detectable loss of mechanical properties on a macroscopic scale. This paper only provides experimental evidence of hydrogen transport by diffusion in pearlitic steel, where hydrogen diffuses towards the points of maximum hydrostatic

stress, its effect being clearly detectable by fractographic analysis after failure.

A final reflection on the evolution of plastic zone in notched samples: in the afore-mentioned cases in which the TTS zone is larger than the plastic zone, the final fracture process is not elastic, but elastic-plastic. The plastic zone analyzed in this paper really means *primary plastic zone*, i.e. that obtained by elastic-plastic FEM analysis *without* introducing the crack generated by the TTS micro-fracture mode. The computation of this primary plastic zone is a first order analysis under *notch plasticity control*. As a matter of fact, there is a secondary plastic zone (PZ*) generated in the vicinity of the crack tip (the TTS zone being considered as an extra-crack prolonging the original notch), so that final fracture by cleavage is initiated in this secondary plastic zone PZ* under *crack tip plasticity control*. However,

the influence of this secondary plastic zone may be assumed to be negligible on hydrogen transport by dislocation sweeping to potential fracture places, since it appears after the development of the TTS crack. With the exception of the shortest tests, this happens at the final stages of loading (within the final 10%), considering the TTS depth at the end of the experiments and the crack growth rate associated with this topography [30]. Therefore, a second order analysis under crack tip plasticity control does not seem to be necessary to obtain reliable conclusions on the interactions between hydrogen and plasticity in this pearlitic steel at the micro-scale. In addition, plasticity can be observed outside the region of calculated plastic zone size, probably due to local stresses or microstructural inhomogeneities, which again could enhance microscopic redistribution of hydrogen over short transport distances.

6. Conclusions

Experimental evidence of hydrogen transport by stress-assisted lattice diffusion in pearlitic steel was provided by means of a fractographic analysis of the region microscopically affected by the hydrogen (TTS) and a numerical study of the evolution of the zone of dislocation movement (PZ), showing that in some cases the hydrogen affected area clearly exceeds the only region where dislocations can move, which in turn seems to demonstrate that stress-assisted diffusion is the predominant mode of transport in pearlitic steel under triaxial stress states produced by notches. The increment of hydrogen absorption produced by the hydrostatic stress at the boundary sample and the accelerating effects of hydrostatic stress gradients in hydrogen diffusion should be taken into account.

These experimental facts are not consistent with dislocation transport of hydrogen and therefore, in spite of the fact that this mode of transport has been sufficiently demonstrated on a microscopic scale, it might not be a critical step for hydrogen embrittlement on a macroscopic scale, detectable with loss of fracture load. Thus hydrogen transport by dislocation dragging is a well established phenomenon, but the question of whether or not it should be considered as an embrittlement mechanism per se still remains open.

Lattice diffusion and dislocation sweeping may be predominant depending on the specific material and external conditions, so any hydrogen embrittlement theory should consider both transport modes. In this framework, and to rationalize hydrogen embrittlement data, it would be extremely important to discriminate the effects of hydrostatic stress fields from those of equivalent stress distributions (related to plastic zone progress) to evaluate the predominant mode of hydro-

gen transport on a macroscopic (continuum mechanics) scale. The same applies to the discrimination between the two commonly competing effects associated with dislocations movement: enhanced transport and enhanced trapping of hydrogen.

Acknowledgements

The financial support of this work by the Spanish DGICYT (Grant UE94-001) and *Xunta de Galicia* (Grants XUGA 11801A93 and XUGA 11801B95) is gratefully acknowledged. In addition, the author wishes to thank Dr V. Kharin (University of La Coruña) for valuable discussions and Mr J. Monar (Nueva Montaña Quijano Company, Santander, Spain) for providing the steel used in the experimental programme.

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