Transmission electron microscopy observations and micromechanical/ continuum models for the effect of hydrogen on the mechanical behaviour of metals

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ABSTRACT

In-situ deformation studies in a transmission electron microscope equipped with an environmental cell have shown that solute hydrogen increases the velocity of dislocations, decreases the stacking-fault energy, and increases the stability of edge character dislocations. Theoretical modelling has established that the hydrogen atmospheres formed at dislocations through the elastic interaction cause a change in the stress field of the dislocation–hydrogen complex in such a manner as to reduce the interaction energy between it and other elastic obstacles. Consequently, solute hydrogen increases the mobility of dislocations, which will be localized to regions of high hydrogen concentration. On the basis of this material softening on the microscale, a solid mechanics analysis of the hydrogen solute interaction with material elastoplasticity demonstrates that localization of the deformation in the form of bands of intense shear can occur on the macroscale. Thus, the present combined experimental and numerical/analytical results provide a clear explanation for the hydrogen-enhanced localized plasticity mechanism of hydrogen embrittlement.

§1. INTRODUCTION

Hydrogen embrittlement is a severe environmental type of failure that affects almost all metals and their alloys. By way of example, one of the many high-symmetry ordered intermetallics, polycrystalline Ni_3Al, exhibits very poor ductility and brittle fracture in the presence of hydrogen or even moist air (Kuruvilla 1985, Bond *et al.* 1989, George *et al.* 1992). Reviewing the voluminous literature on the subject, one may safely summarize that, despite study for 100 years, a complete mechanistic understanding of hydrogen embrittlement has yet to be achieved. Our current understanding leads to the recognition that no single mechanism is responsible for all hydrogen-induced failures (Birnbaum and Sofronis 1994, Birnbaum *et al.* 1997).

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Many mechanisms have been proposed to explain hydrogen-related failure and, as the evidence for and against each mechanism has been extensively reviewed (for example Hirth (1980), Oriani (1987) and Birnbaum et al. (1997)), it is not the purpose to repeat those arguments here but rather to provide the theoretical and experimental evidence for just one mechanism, namely the hydrogen-enhanced localized plasticity (HELP) mechanism (Beachem 1972, Eastman et al. 1981, Tabata and Birnbaum 1984b, Robertson and Birnbaum 1986, Shih et al. 1988, Birnbaum and Sofronis 1994, Ferreira et al. 1998). Evidence for plasticity on hydrogen-induced fracture surfaces has been a common observation for over 30 years and is not an issue of dispute (Beachem 1972, Oriani and Josephic 1974, 1977). What was an issue, and to some extent still remains one, is the significance of the observation of plasticity. Generally, this plasticity was dismissed as an occurrence during or following hydrogen embrittlement rather than a cause of it. This may be attributed in part to the resolution at which the fracture surfaces were examined. At low resolutions, the effects of the localization of the ductility to regions of high hydrogen concentration would not be discernible, giving fracture surfaces a brittle appearance.

Beachem (1972) was the first to propose, on the basis of careful fractography of hydrogen-embrittled steels, that the failure occurred by ductile processes and that hydrogen enhanced and not retarded the mobility of dislocations. This idea was summarily dismissed and ignored until the late 1970s and early 1980s when Robertson, Birnbaum and coworkers (Eastman et al. 1981, Tabata and Birnbaum 1984b, Robertson and Birnbaum 1986, Bond et al. 1987, 1988, 1989, Shih et al. 1988, Hanninen et al. 1993, Ferreira et al. 1998) and independently Lynch (1979, 1988) revived Beachem's mechanism. Robertson, Birnbaum and co-workers provided direct observation of the dislocation velocity enhancement due to hydrogen by deforming materials in situ in a transmission electron microscope equipped with an environmental cell. Lynch (1979, 1988) proposed, on the basis of high-resolution fractography and the similarity of liquid metal and hydrogen-embrittled fracture surfaces, that hydrogen enhanced the injection of dislocations from the surface. What distinguishes these dislocation mechanisms is the location of the enhancement, which in Lynch's model occurs at the surface and in the model of Robertson, Birnbaum and co-workers throughout the material.

In this paper, we first review the experimental evidence demonstrating that hydrogen enhances dislocation mobility on the microscale and then use a micromechanics approach to explain that the enhanced dislocation mobility is due to the hydrogen-induced shielding of the interactions between dislocations and elastic obstacles. Finally, a continuum mechanics approach will be used to show that hydrogen-induced softening on the microscale can lead to shear localization of the plastic flow on the macroscale.

§2. EXPERIMENTAL EVIDENCE FOR HYDROGEN-ENHANCING DISLOCATION MOBILITY

A controlled environment transmission electron microscope permits gas–solid interactions to be observed in real time and at a high spatial resolution; the design of such a facility has been described by Lee et al. (1991) and Robertson and Teter (1998). Straining stages for use in this microscope permit deformation experiments to be performed in gaseous environments, allowing for direct observation of the embrittlement effect, albeit in an electron-transparent specimen. The samples used are of a simple rectangular geometry with dimensions of 10 mm × 3 mm × 0.150 mm.

The central portion of these samples is thinned to electron transparency using conventional thinning techniques.

The series of images shown in figure 1 were captured as individual frames from a videotape and illustrate the change in the dislocation structure as the hydrogen pressure in the environmental cell and, hence, the concentration in the sample, increases. The dislocations were produced by deforming the material in vacuum. The load was then held constant and hydrogen gas introduced so that any changes resulted solely from the introduction of the gas; it is important to note that gases other than hydrogen were introduced but hydrogen was the only gas to cause such motion. The motion continues for periods longer than the equilibration time, which is consistent with the fact that the effect is not due to the stress field generated from the hydrogen concentration gradient at the surface. The dislocation motion could be stopped and started simply by removing and reintroducing the gas from the environmental cell and, hence, from the sample. Similar observations have been made in a wide range of materials with different crystal structures: iron (Tabata and Birnbaum 1984a), nickel (Robertson and Birnbaum 1986), steels (Rozenak *et al.* 1990, Hanninen *et al.* 1993), aluminium and aluminium alloys (Bond *et al.* 1987, 1988), titanium and titanium alloys (Shih *et al.* 1988) and Ni_3Al (Bond *et al.* 1989). Hydrogen-enhanced dislocation mobility has been observed for perfect edge, screw and mixed dislocations as well as for partial dislocations. These generalities suggest that the responsible mechanism has to be universal and not particular to any crystal structure or dislocation type.
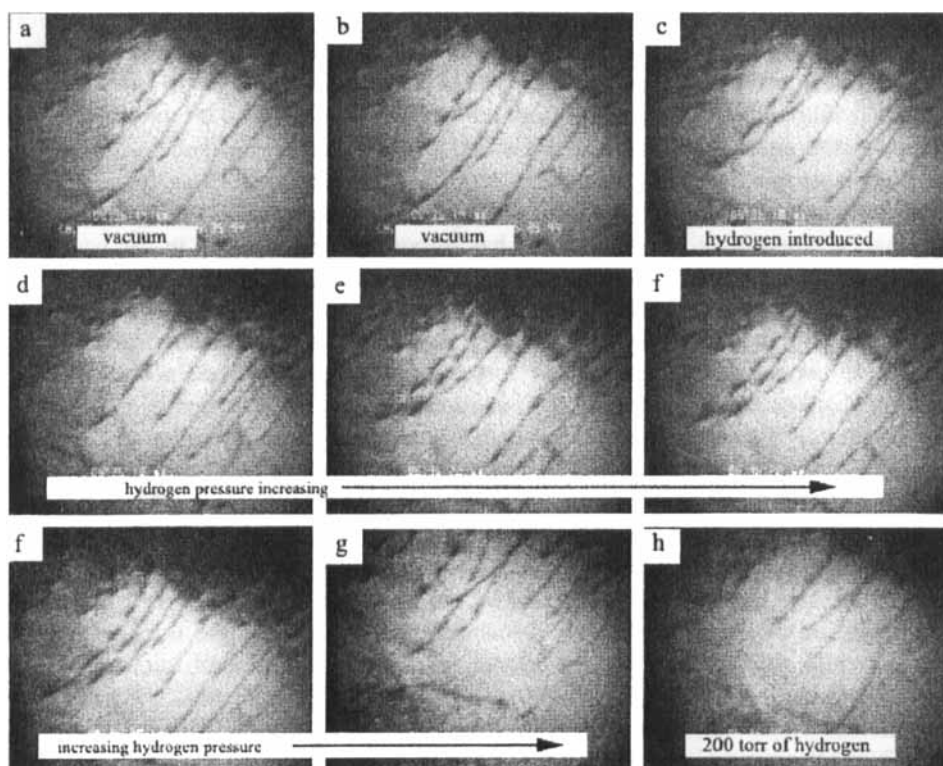

Figure 1.   Dislocation motion induced by the introduction of hydrogen gas into the environmental cell and, hence, into the sample. The material is iron.

The above observations were made in thin (less than 200 nm thick) electron-transparent foils, which raises the question about surface effects. Supporting experimental observations on bulk materials are available in the form of stress drop and strain-rate change mechanical property tests on Ni (Sirois and Birnbaum 1992) and type 310s stainless steels (Abraham and Altstetter 1995). These bulk studies showed a reduction in the activation area and activation enthalpy for dislocation motion in the presence of hydrogen, which is consistent with the facts that hydrogen reduces the interaction energy between dislocations and obstacles and ultimately increases the mobility of dislocations.

These experimental observations were the driving force for modelling the influence of hydrogen on the stress field of dislocations and other elastic obstacles.

§ 3. HYDROGEN SOLUTE INTERACTION WITH ELASTIC DEFORMATION

The total elastic interaction energy between a solute atom and a dislocation consists of two components. The first component is a first-order elastic interaction energy (Cottrell 1948, Eshelby 1957) associated with the lattice dilatation when a hydrogen solute is introduced against a stress field. The other is a second-order interaction that results from the additional change in the potential energy due to the change in the moduli upon the introduction of the stress centre (solute atom) in the lattice while the external stresses are held fixed. In general, the second-order interaction energy is much smaller than the first-order interaction energy. In the vicinity of a dislocation, the second-order interaction energy decreases with distance from the dislocation as $1/r^2$ in contrast with the $1/r$ dependence of the first-order interaction energy. In a linearly elastic isotropic material, the first-order interaction dominates all solute interactions with edge dislocations. It also dominates the interaction between screw dislocations and solutes having distortion fields with symmetries lower than cubic (e.g. carbon interstitials). The second-order interaction energy dominates the interaction between screw dislocations and solutes such as hydrogen that have isotropic distortion fields (e.g. hydrogen interstitials). Thus, for a linearly elastic isotropic material, a hydrogen atmosphere develops more readily around an edge than a screw dislocation, and this has important implications in the way that hydrogen influences the dislocation character (Ferreira *et al.* 1998).

To assess the effect of this hydrogen atmosphere on the interaction energy, the case of two similar edge dislocations on the same slip plane was considered. In the absence of hydrogen, the interaction force per unit length between two parallel edge dislocations with the same sign is repulsive (Hirth and Lothe 1982). The dependence of the shear stress, normalized by the shear modulus μ, on the separation distance between the dislocations, normalized by the magnitude of the Burgers vector of the dislocations, is shown for two similar edge dislocations on the same slip plane in figure 2 (*a*). The hydrogen effect on the interaction between dislocations 1 and 2 is assessed by calculating the hydrogen-induced change in the shear stress. The shear stress τ_H induced by the hydrogen atmosphere is found from the calculation of the relaxed elastic stress field associated with the introduction of hydrogen into the lattice while the elastic moduli are allowed to vary pointwise according to the local hydrogen concentration. These stress fields, which are negative and increase as the absolute hydrogen concentration increases, are also shown in figure 2 (*a*) for an initial hydrogen concentration of 0.1 atoms per solvent atom. The total stress field in the lattice is found by superposition of the relaxed elastic stress due to hydrogen, and that of the standard singular elastic dislocation stress field
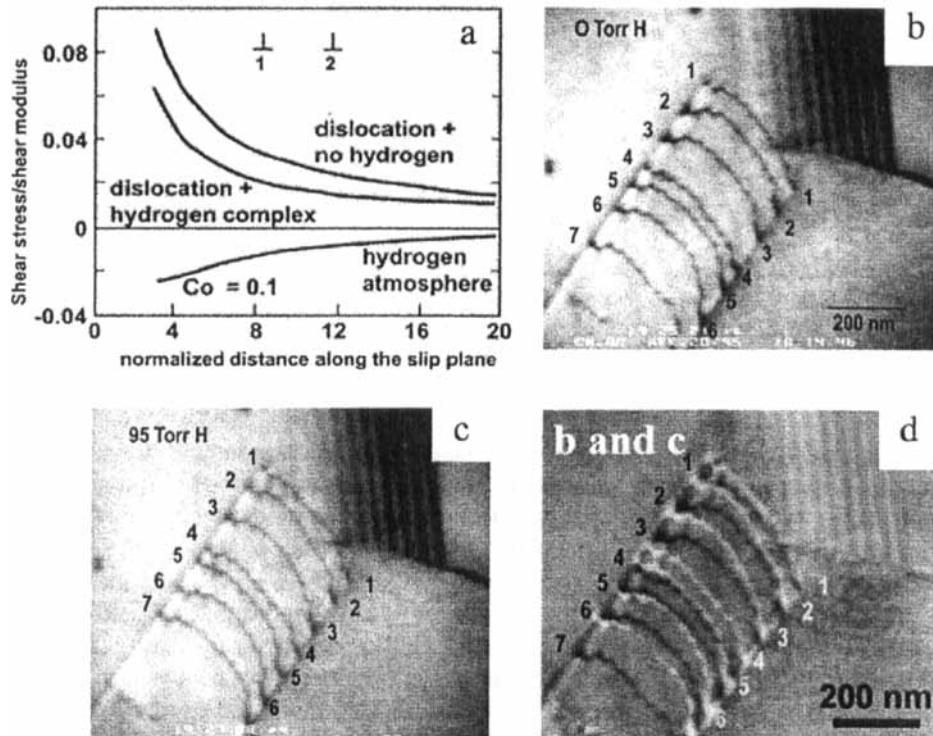
Figure 2. Hydrogen-shielding model: (*a*) plot of the normalized shear stress as a function of separation distance for two edge dislocations on the same slip plane with and without hydrogen atmospheres; (*b*) dislocation pile-up at a grain boundary in type 310s stainless steel; (*c*) effect of introducing hydrogen gas at 90 Torr on the dislocation pile-up; (*d*) comparison image made from superimposing the negative image in (*c*) on the positive image in (*b*).

(Sofronis and Birnbaum 1995). As shown in figure 2 (*a*), the effect of hydrogen is to decrease the repulsive force between the two edge dislocations. A similar reaction would occur between an edge dislocation and any elastic obstacle.

A consequence of this hydrogen-shielding model is that the equilibrium separation distance between dislocations in a pile-up will decrease when hydrogen is introduced into the system. This effect has been observed experimentally in stainless steel and an example is shown in figures 2 (*b*)–(*d*) (Ferreira *et al.* 1998). The dislocation pile-up against the grain boundary was created by deforming the sample in vacuum. The load was then held constant and hydrogen gas introduced into the system. With the introduction of hydrogen the dislocations moved closer to the obstacle and to each other. This change can be seen by comparing figures 2 (*b*) and (*c*), which respectively show the initial position of the dislocations and their position after hydrogen gas at 90 Torr has been introduced into the environmental cell. The change in dislocation position is more apparent in the comparison image (figure 2 (*d*)), which was formed by superimposing a negative image of the dislocation structure in hydrogen gas at 90 Torr (white dislocations) (figure 2 (*c*)) and a positive image of the original position (figure 2 (*b*)). While these observations were made in a thin electron-transparent foil, the mechanical property measurements on bulk Ni–C–H alloys (Sirois and Birnbaum 1992) showed a decrease in the 'activation enthalpy' for

Hydrogen pressure increased   Hydrogen pressure decreased   Hydrogen pressure increased
from 9 to 70 torr   from 70 to 15 torr   from 9 to 70 torr
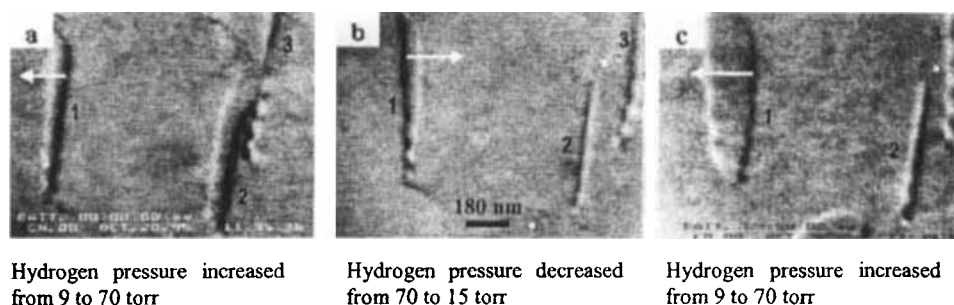
Figure 3.   Reversibility of dislocation motion on the addition and removal of hydrogen. The material is high-purity aluminium.

slip (corresponding to the decrease in the calculated interaction energy with hydrogen) and a decrease in the 'activation volume' (corresponding to the decrease in the width of the activation energy minimum) when hydrogen was present. The thin-foil observations and the mechanical property results are fully consistent with the fact that hydrogen influences the dislocation mobility. Hydrogen-shielding effects were also studied for the interaction of screw dislocations in the bcc lattice (Sofronis and Birnbaum 1995). Hydrogen effects on the interaction energy in this case result from the local moduli changes due to the hydrogen atmosphere around the carbon interstitial. Experimentally hydrogen has been observed to influence the mobility of screw dislocations in iron, with the effect being greater in high-carbon-content materials (Tabata and Birnbaum 1984a).

The underlying principle of the hydrogen-shielding mechanism is that hydrogen diminishes the local stress field of dislocations and solute impurities and this permits dislocations to move together with their hydrogen environments at lower applied stresses. The effect must be reversible in that, when the hydrogen is removed from the sample, the dislocations within the pile-up must move further apart. Figure 3 shows a series of comparison images with the negative image (white dislocations) showing the response of increasing or decreasing the hydrogen concentration. From these images it is clear that by changing the hydrogen pressure the dislocations can be made to move forwards or backwards. That is, the direction of motion changes in relation to the changes in hydrogen concentration (Ferreira et al. 1998).

§4. Hydrogen effect on shear localization of the plastic flow

In the preceding section a theoretical explanation and experimental confirmation of the shielding mechanism of hydrogen-enhanced plasticity were presented. These effects will be confined to, and be more prevalent in, regions of high hydrogen concentration, which will tend to localize the effects. Localization effects due to hydrogen have been observed in a number of bulk studies (Onyewuenyi 1984, Bernstein and Dollar 1988, Deve et al. 1989, Hicks and Altstetter 1992, Tien and Altstetter 1993, Abraham and Altstetter 1995). In this section a theoretical explanation is presented for the onset of the shear localization in the presence of hydrogen (Sofronis et al. 2001). Hydrogen is assumed to reside at normal interstitial lattice sites (NILS) or reversible trapping sites at microstructural defects generated by plastic deformation. Interstitial hydrogen populations are qualified by the hydro-

static stress whereas the trapped hydrogen populations develop always in equilibrium with NILS hydrogen (Taha and Sofronis 2001) as dictated by Oriani's (1970) theory. The number of traps is assumed to vary proportionally to the dislocation density, which is assumed to vary linearly with the plastic strain. The model assumes one trapping site per atomic plane threaded by a dislocation. Thus the total hydrogen concentration (in trapping sites and NILS) can be determined as a function of both the hydrostatic stress and the equivalent plastic strain ε^P in the form $c = c(\sigma_{kk}, \varepsilon^P)$, where c is measured in hydrogen atoms per solvent atom. Based on the fact that hydrogen increases the dislocation mobility, one may suggest that the hydrogen effect on the local flow stress σ_Y can be stated as $\sigma_Y = \sigma_0^H (1 + \varepsilon^P/\varepsilon_0)^{1/n}$, where σ_0^H is the initial yield stress in the presence of hydrogen that decreases with increasing hydrogen concentration (Sofronis *et al.* 2001), ε_0 is the initial yield strain in the absence of hydrogen, ε^P is the logarithmic strain in uniaxial tension and n is the hardening exponent that is assumed to be unaffected by hydrogen.

For the plastic response in the presence of hydrogen, the material is assumed to flow according to the von Mises J_2 flow theory and to harden isotropically. Thus (Sofronis *et al.* 2001),

$$D_{ij}^p = \frac{1}{h}\left(\frac{3\sigma_{kl}'}{2\sigma_e} + \mu\delta_{km}\delta_{lm}\right)\frac{3\sigma_{ij}'\overset{\triangledown}{\sigma_{kl}}}{2\sigma_e} \tag{1}$$

is the plastic component of the rate of the deformation tensor, $\sigma_e = (3\sigma_{ij}'\sigma_{ij}'/2)^{1/2}$ is the von Mises equivalent stress, $\sigma_{ij}' = \sigma_{ij} - \sigma_{kk}\delta_{ij}/3$ is the deviatoric stress,

$$h = \partial\sigma_Y/\partial\varepsilon^P + (\partial\sigma_Y/\partial c)(\partial c/\partial\varepsilon^P),$$

$$\mu = -(\partial\sigma_Y/\partial c)(\partial c/\partial\sigma_{kk}),$$

$$\varepsilon^P = \int (2D_{ij}^p D_{ij}^p/3)^{1/2}\,dt$$

is the effective plastic strain, δ_{ij} is the Kronecker delta, the summation convention is used over a repeated index, and the superposed $\triangledown$ denotes the Jaumann stress rate that is spin invariant. Following Rudnicki and Rice (1975) and Rice (1976), one finds that localization of the plastic flow is possible when the hardening modulus h reduces upon loading to a critical value that depends on the local stress and factors such as c, $\partial c/\partial\varepsilon^P$, $\partial c/\partial\sigma_{kk}$, $\partial c/\partial\sigma_Y$ and the elastic moduli (Sofronis *et al.* 2001). The localization condition was studied by solving the elastoplastic boundary value problem coupled with the calculation of the hydrogen concentration in the case of a niobium specimen stressed in uniaxial tension under plane strain conditions. Figure 4 shows the normalized true (logarithmic) strain $\varepsilon_{22}/\varepsilon_0$ at localization plotted against the initial hydrogen concentration c_0 for work-hardening exponents $n = 5$ and $n = 10$ and yield stress $\sigma_0 = 400\,\text{MPa}$. The effect of hydrogen causes the critical modulus for localization to be positive. The model is based on hydrogen-induced material softening and lattice dilatation, both of which have been experimentally verified. The numerical results seem to overestimate the macroscopic strain required for localization as predicted by experiments. It is, however, well known that the von Mises flow theory dramatically overestimates the bifurcation strain. Furthermore, the calculated hydrogen effect can be intensified quantitatively by considering more effective trapping modes of hydrogen such as in the form of atmospheres in the presence of higher stress triaxialities such as those ahead of a crack tip.
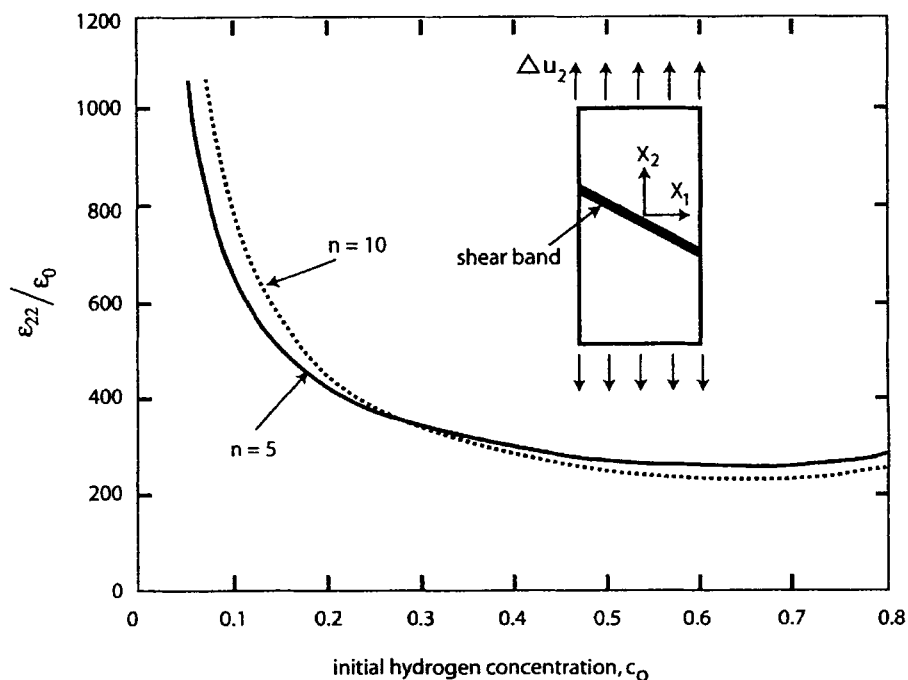
Figure 4. Macroscopic strain at the onset of localization versus initial hydrogen concentration.

§5. CONCLUSIONS

A theoretical framework for explaining the experimentally observed mechanism of hydrogen enhancement of the dislocation mobility has been presented. This mechanism must therefore be accounted for in life prediction models of hydrogen embrittlement. It must be appreciated that this is just one of the viable mechanisms of hydrogen embrittlement and it will probably dominate only when certain conditions prevail. Hydrogen-induced decohesion and stress-induced hydride formation and cleavage will also occur under appropriate circumstances and it is likely that more than one mechanism may operate within a given system.

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