

# MECHANICS MODELS FOR HYDROGEN EMBRITTLEMENT MECHANISMS

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## ABSTRACT

Of the many suggestions of hydrogen-induced degradation of engineering materials, two mechanisms appear to be viable in non-hydride forming systems: hydrogen-enhanced localized plasticity (HELP) and hydrogen-induced decohesion.

The present work attempts to link the experimentally observed hydrogen-enhanced dislocation mobility and lattice dilatation to shear localization and ductile rupture processes at the macroscale in the presence of hydrogen. Plasticity models accounting for the hydrogen effects at the microscale are used to study the conditions under which hydrogen induces shear banding in a specimen under plane-strain tension. It is demonstrated that hydrogen induces loss of ellipticity in the governing rate equations of the macroscopic material deformation. Studies on the crack-front constraint variations indicate that the resistance to ductile fracture of low and high constraint configurations depends on the initial hydrogen concentration and the associated amount of softening. On the basis of the Rice and Tracey model for void growth, it is demonstrated that the fracture process ahead of a crack tip in the presence of hydrogen is strongly controlled by the plastic strain in agreement with the HELP mechanism for embrittlement.

In contrast, one of the earliest and most often cited theories of hydrogen embrittlement is the decohesion theory, which is based on the postulate that solute hydrogen decreases the force required to separate the crystal along a crystallographic plane, grain boundary or a particle/matrix interface. Decohesion along grain boundary carbides is believed to be a form of hydrogen-induced degradation, also observed experimentally in Ni-base alloy 690. A coupled model of transient hydrogen transport through a plastically deforming matrix with elastic precipitates and debonding particle/matrix interfaces is presented. The numerical results indicate that hydrogen reduces both the macroscopic stress and strain for internal void nucleation.

## 1 INTRODUCTION

The purpose of this work is to simulate the plastic deformation of materials in the presence of hydrogen from a continuum mechanics viewpoint in an effort to increase our understanding on how hydrogen affects deformation stability, void growth, and decohesion. The hydrogen effect on shear localization is studied in a plane strain specimen under tension. The condition for bifurcation of the homogeneous deformation into a mode of intense shear banding is monitored in time as the load increases. The interaction of hydrogen with the elastic  $T$ -stress is used to understand the combined effect of hydrogen and the crack tip front constraint on void growth ahead of a blunting crack tip. The calculations show that this interaction is rather complex, shallow crack configurations can be severely degraded by hydrogen, and deep-notch specimens do not necessarily provide a conservative toughness assessment in the presence of hydrogen. In both studies, the amount of hydrogen in the specimen is calculated by considering the extent of plastic straining (trapped hydrogen) and hydrostatic stress (hydrogen in normal interstitial lattice sites). In view of the very high mobility of the hydrogen solute, hydrogen concentration in trapping sites is assumed always to be in equilibrium with hydrogen in interstitial sites, which is also assumed to be in equilibrium with local hydrostatic stress. The calculated hydrogen

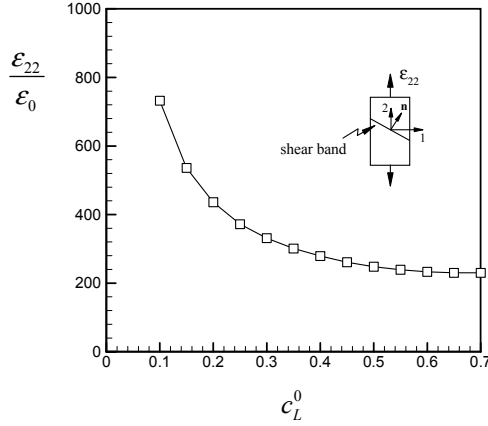


Fig. 1: Critical normalized macroscopic strain  $\epsilon_{22}/\epsilon_0$  for the onset of shear localization against the initial hydrogen concentration  $c_L^0$  in lattice interstitial sites measured in hydrogen atoms per solvent atom (H/M).

concentration (pointwise) is then used to estimate the amount of material softening (pointwise) as reflected in the corresponding local flow stress along the lines of the experimental observations by Tabata and Birnbaum [1]. The idea is that by accounting for the hydrogen effect on the material constitutive law, one can study the conditions for the onset of plastic instability and for the development of the stress and deformation fields ahead of a blunting crack tip. The effect of hydrogen on interfacial decohesion is studied by simulating hydrogen-induced separation at a particle/matrix interface and grain boundaries in nickel-base alloy 690. Unlike the studies on shear localization and constraint effects, the analysis for alloy 690 is based on transient stress-driven hydrogen transport.

The material is assumed to be rate-independent, yield according to the von Mises criterion, and harden isotropically during plastic straining. The associated flow rule is given by  $\overset{\nabla}{\sigma}_{ij} = L_{ijkl} D_{kl}$ , where the superposed  $\nabla$  denotes the Jaumann rate of stress,  $D_{ij}$  is the symmetric part of the velocity gradient, the tensor  $L_{ijkl}$  of the elastoplastic constitutive moduli [2,3] depends on the current state of stress, the hydrogen concentration, and the work hardening characteristics of the material, and the standard summation convention is implied over a repeated index. It is worth noting that the hydrogen effect makes yield to be sensitive to pressure and the overall dilatation to have a plastic component [2].

## 2 EFFECT OF HYDROGEN ON SHEAR LOCALIZATION

It is well known that the onset of bifurcation from homogeneous deformation into a band of intense shear flow takes place when the equations governing incremental equilibrium lose their ellipticity. In other words, at the state of loading at which a critical change in the constitutive moduli  $L_{ijkl}$  is impending, an additional increment of load is accommodated not by continued homogeneous deformation but by a localized deformation in a band of intense shear instead. For a homogeneous solid, the condition for bifurcation of the homogeneous deformation into a mode of intense shear banding is stated as [2]

$$\det[n_k L_{kijl} n_l + A_{ij}] = 0, \quad (1)$$

where  $\mathbf{n}$  is the unit vector normal to the direction of the forming shear band (see inset of Fig. 1),  $A_{ij} = (-\sigma_{ij} + \sigma_{ik}n_kn_j + \sigma_{kl}n_kn_l\delta_{ij} - \sigma_{mj}n_in_m)/2$ , and  $\delta_{ij}$  is the Kronecker delta. Condition (1) for shear localization was studied in the case of a niobium specimen undergoing incremental homogeneous tension in plane strain. Niobium was chosen as data are readily available. The localization condition was studied by solving the elastoplastic boundary value problem coupled with the calculation of the hydrogen concentration as straining progresses and the hydrogen concentration changes. The critical applied macroscopic strain  $\varepsilon_{22}/\varepsilon_0$  at which shear localization commences is shown plotted against the initial hydrogen concentration  $c_L^0$  measured in hydrogen atoms per niobium atom in Fig. 1. In uniaxial tension and in the absence of hydrogen,  $\sigma_0$  is the yield stress,  $E$  the Young's modulus, and  $\varepsilon_0 = \sigma_0/E$ . The results show that hydrogen by affecting the material constitutive response triggers shear localization under plane strain tension. The localization is triggered despite the fact that the specimen continues to harden macroscopically. It is emphasized that shear localization is not possible in the absence of hydrogen under plane strain tension with such hardening material. Also, it is worth noting that the numerical results overestimate the macroscopic strain required for localization as predicted by experiments [1]. 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.

### 3 EFFECT OF HYDROSTATIC CONSTRAINT ON VOID GROWTH

Deeply cracked geometries are known to have a positive  $T$ -stress and a fracture toughness in the absence of hydrogen that falls below the toughness measured in negative  $T$ -stress geometries, that is, in shallow notch specimens. In the presence of hydrogen the fracture toughness of these geometries was investigated by studying the combined effect of  $T$ -stress, hydrogen-induced dilatation, and hydrogen-induced softening on void growth in a niobium system [4]. The study was carried out at a blunting crack tip under plane strain loading and small scale yielding conditions. Solutions of the boundary value problems furnish hydrogen-modified values of the strain and stress fields ahead of the crack tip that are used to assess void growth via the classical model of Rice and Tracey. By neglecting the void interaction effects, a simple point-wise descriptor of void growth ahead of a crack tip is the parameter

$$\zeta(t) = \ln\left(\frac{R}{R_0}\right) = \int_0^t B \dot{\varepsilon}^p \exp\left(\frac{3\sigma_m}{2\sigma_e}\right) dt' \quad (2)$$

which was calculated as a function of time  $t$  (load) and position in the neighborhood of the crack tip. In eqn (2), the parameters  $R$  and  $R_0$  denote the void radius respectively at times  $t$  and zero,  $\dot{\varepsilon}^p$  is the effective plastic strain rate,  $\sigma_m = \sigma_{kk}/3$  is the hydrostatic stress,  $\sigma_e$  is the Mises effective stress, and  $B$  is a constant often taken as 0.283. In Fig. 2 the non-dimensionalized growth parameter  $\bar{\zeta} = \zeta/\zeta_{ref}$  is shown plotted for various initial hydrogen concentrations,  $T$ -stress level, and material softening, where  $\zeta_{ref}$  is the value of  $\zeta$  at the reference state of zero  $T$ -stress and no hydrogen.

In the *absence of hydrogen*, a positive (negative)  $T$ -stress accelerates (retards) void growth over  $X\sigma_0/J > 0.37$  and slightly retards (accelerates) void growth for  $X\sigma_0/J < 0.37$ , where the applied load is measured in terms of the  $J$  integral value. Since the  $T$ -stress affects both the

hydrostatic stress and the effective plastic strain, void growth in the absence of hydrogen is both stress and strain controlled. In the *presence of hydrogen* but with no softening ( $\xi=1$ ), Fig. 2a shows that when  $T=0$  hydrogen acting as a dilatation stress center ahead of the crack tip retards void growth by reducing the plastic strain more than it increases the hydrostatic stress. Figs. 2b and 2c indicate that a positive (negative)  $T$ -stress reduces (increases) the effective plastic strain, and thus hydrogen suppresses (enhances) void growth at large  $c_L^0$  (e.g. 0.01 H/M). These effects which are opposite to those by the  $T$ -stress in the absence of hydrogen are strain-controlled. *Hydrogen-induced softening* decreases the hydrostatic stress and increases the effective plastic strain relative to the values dictated by the interaction of positive or negative  $T$ -stress with hydrogen-induced dilatation. Figs. 2b and 2c show that hydrogen-induced softening increases void growth and this is a strongly strain-driven effect. Notice that for  $c_L^0=0.001$  H/M and  $T/\sigma_0=0.4$  with  $\xi=-49$  (5% reduction of the yield stress) both the  $T$ -stress and hydrogen-induced softening effects contribute toward void enlargement whereas for  $c_L^0=0.01$  H/M,  $T/\sigma_0=0.4$  and with  $\xi=-4$  (5% reduction of the yield stress) softening counteracts the combined effect of  $T$ -stress and hydrogen-induced dilatation on decreasing void growth. For negative  $T$ -stress, Fig. 2c shows that softening reinforces the combined effect of  $T$ -stress and hydrogen-induced dilatation on increasing void growth.

These results indicate that for positive  $T$ -stress geometries and at an initial hydrogen concentration of  $c_L^0=0.001$  H/M hydrogen can lead to substantially enhanced void growth and

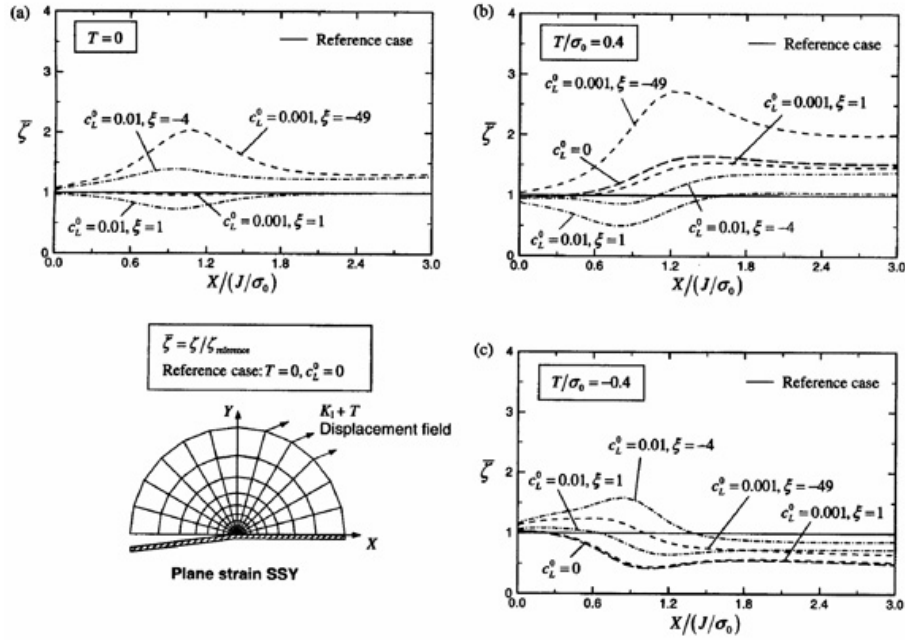


Fig. 2: Void growth parameter  $\bar{\zeta}$  ahead of a crack tip at various values of  $c_L^0$ ,  $\xi$ , and  $T$ . The parameter  $\xi$  controls softening through the yield stress  $\sigma_0(c) = [(\xi-1)c+1]\sigma_0$ , where  $c = c_L + c_T$  is the number of hydrogen atoms in lattice sites,  $c_L$ , and traps,  $c_T$ , per solvent atom.

hence substantial fracture toughness reduction relative to the reference case of zero  $T$ -stress and no hydrogen. For negative  $T$ -stress geometries, hydrogen also enhances void growth and reduces fracture toughness with increasing initial hydrogen concentration relatively to the reference case. *In fact for these geometries, there is a synergism of hydrogen dilatation, softening, and constraint toward enhancing void growth.* Note that at an initial hydrogen concentration of 0.001 H/M and with a degree of softening of 5% Figs. 2b and 2c indicate that in the presence of hydrogen the low constraint configuration exhibits more resistance to degradation than the high constraint one. In general though, the deep-notch toughness data in the presence of hydrogen need not necessarily lead to a conservative fracture toughness assessment for shallow cracked geometries as is commonly assumed in the absence of hydrogen (e.g. cases with  $c_L^0 = 0.001$  H/M and  $\xi = -49$  in Fig. 2).

The combined effect of hydrogen-induced dilatation, softening, and constraint on fracture toughness reduction by void growth is governed by the hydrogen-induced increase of the plastic straining. Hence the present work argues for a fracture process in the presence of hydrogen that is controlled by the plastic strain. This model of hydrogen induced degradation is in agreement with the HELP mechanism for embrittlement with the fracture event taking place by void growth and coalescence. As has been discussed, in negative  $T$ -stress geometries the effect of hydrogen is reinforced by the constraint and softening in reducing the fracture toughness of the material. Therefore, negative  $T$ -stress configurations can be used in a systematic way by varying the initial hydrogen concentration to study the hydrogen effect on material degradation.

#### 4 HYDROGEN-INDUCED DECOHESION IN NICKEL-BASE ALLOY 690

As has been demonstrated by Symons [5], hydrogen embrittlement of cylindrical tensile or notched bend specimens of nickel-base alloy 690 is characterized by a predominantly intergranular fracture mechanism that involves microvoid initiation at grain boundary carbides followed by growth and coalescence. To study the effect of hydrogen on void nucleation at a particle/matrix interface, finite element calculations were carried out in which transient hydrogen transport toward and along the interface was coupled with bulk material elastoplastic deformation and interfacial decohesion [3].

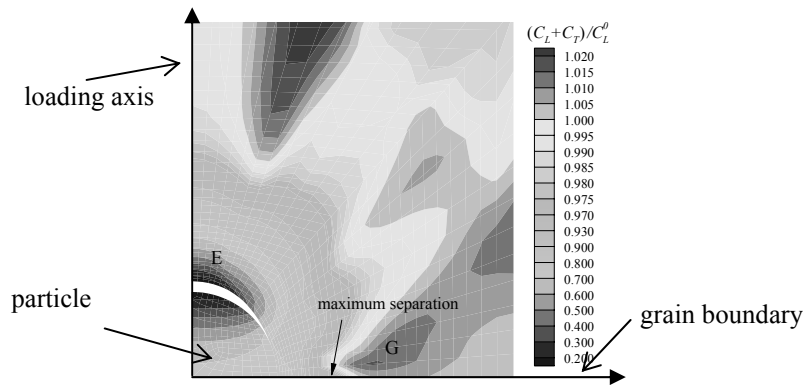


Fig. 3: Hydrogen distribution in the first quadrant of the unit cell at macroscopic strain 0.0705 . The macroscopic strain rate was constant and equal to  $4.0 \times 10^{-4}$  /s . Concentrations  $C_L$ ,  $C_T$ , and initial concentration  $C_L^0$  are measured in hydrogen atoms per unit volume.

The simulations were carried out at a unit cell containing a cylindrical inclusion loaded in plane-strain tension at a uniform initial hydrogen concentration of 30wppm and for material data for the nickel-base alloy 690. The cell also contained a grain boundary normal to the axis of loading and capable of undergoing hydrogen-affected separation (Fig. 3). The hydrogen effect on interfacial cohesion was modeled by a phenomenological law built on the thermodynamic description of interfacial cohesion of Hirth and Rice [6] and implemented through a cohesive finite element methodology [7].

Fig. 3 shows a debonded segment of the particle/matrix interface (P/MI). The opened interfacial crack acts as a sink for the hydrogen solutes that depletes the surrounding area of its hydrogen, as is shown for the area containing point E. Further, as this crack gets larger, load transfer to the matrix above the grain boundary induces a local hydrostatic stress intensification which attracts hydrogen to the area centered at point G. The cell fails by complete grain boundary decohesion at macroscopic strain 0.0705 at which the normal traction on the unit cell diminishes abruptly to zero. The combination of local stress concentration and high value of the hydrogen trapping energy along the P/MI yields interfacial hydrogen segregations that are an order of magnitude greater than the grain boundary segregations. *As a consequence, the cohesion of the P/MI is reduced by hydrogen to a much greater extent than the cohesion of the grain boundary.* So the process of cell failure is initiated by an interfacial decohesion close to the top of the particle which produces a debonded interfacial segment propagating toward the grain boundary. This intensifies the stress elevation along the grain boundary which in turn is followed almost instantaneously by complete failure of the entire grain boundary.

## 5 CONCLUSIONS

- i) Hydrogen-induced material softening at the microscale has been shown to promote plastic flow localization at the macroscale under plane strain tension.
- ii) The common assumption that deep-notch toughness data provide conservative toughness assessment for low constraint configurations may not be true in the presence of hydrogen.
- iii) Hydrogen-induced degradation of alloy 690 is void-nucleation controlled and promoted by reduction of the cohesive strength at grain boundary carbides.

## ACKNOWLEDGMENTS

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