HYDROGEN DAMAGE IN THE CRACK TIP ENVIRONMENT

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ABSTRACT

This paper assesses the implications of recent investigations into crack tip stresses and deformation in deformable materials, critical for modeling hydrogen-affected cracking. Results from conventional J_2 plasticity theory, the present foundation of modeling hydrogen-influenced cracking, are contrasted with crack tip models which incorporate microstructural features: dislocation free zone models, strain gradient models, and discrete dislocation simulations. An important result is that models with explicit microstructure predict near tip stresses that are significantly higher than those predicted via conventional continuum plasticity. This has profound implications for hydrogen-assisted cracking, for three reasons: (*i*) the concentration of reversibly trapped and mobile H, enriched by high-local hydrostatic stresses, exceeds that of trapped hydrogen alone, (*ii*) the length over which high H concentrations exist is larger, and (*iii*) high-local stresses more readily achieve decohesion. The ability of microstructurally-grounded plasticity descriptions to rationalize large concentrations of hydrogen over relatively large length scales implies that H-induced change in cohesive strength is reasonable .

1. INTRODUCTION

Hydrogen promotes subcritical crack growth in high strength iron, nickel, aluminum and titanium-based alloys, by hydrogen environment embrittlement (HEE) and internal hydrogen embrittlement (IHE) [1]. HEE involves concurrent and damaging interaction of (electro)chemically produced atomic hydrogen (H) and crack tip stress, while IHE involves crack tip embrittlement from predissolved H and stress. Both damage modes likely involve the same embrittlement physics; be it H-reduced cohesive strength, H-enhanced localized plasticity, or brittle hydride formation. The threshold stress intensity for the onset of IHE and HEE, K_{TH}, is governed by the local interaction of trapped H and normal stresses focused in the crack tip fracture process zone (FPZ). The FPZ location varies with source of embrittling H, either the crack surface for HEE or surrounding microstructure for IHE. The rate of subcritical crack growth, da/dt, is governed by production and transport of H to such sites [2]. These kinetics differ for IHE and HEE due to different H distributions. A central challenge in managing and mitigating IHE and HEE is to model K_{TH} and da/dt from the crack tip damage mechanism perspective. In these formulations, several elements must be quantified, including [2,3]:

- Distributions of normal and hydrostatic stresses, e.g. the opening direction normal stress (σ_{YY}) for the Mode I crack configuration.

- Hydrogen concentration at trap sites that constitute the brittle path through the microstructure, given by lattice-dissolved H adjacent to the trap amplified by an exponential dependence on H-trap binding energy, E_B. In addition to solute, vacancies and microstructural interfaces, dislocations from crack tip deformation trap H.

- Enhanced lattice H content due to hydrostatic stress (σ_H) about the crack tip, given by the normal lattice concentration amplified by an exponential dependence on the stress field interaction energy (dictated by σ_H and partial molar volume of H in the metal).

- Failure criterion, specific to the damage mechanism and involving the intrinsic strength of damage sites, reduced by the presence of elevated H concentration, and acted on by the maximum σ_{YY} in the FPZ.

Three monumental challenges have confounded the hydrogen embrittlement community for the past four decades [1]. The basic H-damage mechanism is controversial, the amount of H produced on a straining-reacting crack tip surface in HEE is challenging to measure or model, and the proper mechanics description of crack tip stresses is uncertain. The objective of this paper is to critically assess the proper description of crack tip stresses, with emphases on defining the microstructure and/or damage process length scale dependence of stress and the associated effect on the concentration of H local to the crack tip.

2. CRACK TIP STRESS: BACKGROUND

Rice proposed the elastic-plastic fracture mechanics approach that has provided the foundation for modeling hydrogen-affected cracking over the past two decades [3,4]. The Hutchinson-Rice-Rosengren (HRR) asymptotic field describes stresses and strains within the crack tip plastic zone, controlled by the J-integral and augmented by large strain finite element analysis by McMeeking and others [5]. The critical features of this approach are illustrated by the curve *"J_2: blunt crack"* in Fig. 1. The J_2 result reflects a blunt crack tip with an opening, $\delta_T \sim K^2/(2\sigma_Y E)$. For high strength alloys, $\sigma_Y \sim \sigma_{flow}$, K is the elastic-far field stress intensity and E is elastic modulus. The distance from the crack tip has been normalized by a material length scale, ~1 μm, as discussed in subsequent sections. The stress increases from the uniaxial yield strength σ_Y at the crack tip surface, through a maximum at a distance ahead of the crack tip given by $\sim J/\sigma_Y \sim K^2/(\sigma_Y E)$, and merges with the HRR stress. The σ_H distribution mirrors the σ_{YY} trend. For high strength and low work hardening alloys, the maximum levels of σ_{YY} and σ_H are about *3.5σ_Y* and *2.5σ_Y*, respectively [5,6].

The blunt crack solution may not be relevant to H cracking in high strength alloys. Recent studies of crack tip behavior have focused on quasi-ductile cleavage, wherein atomistic or crystallographic decohesion occurs in the presence of significant plastic deformation. Ignoring for the moment the role of H, the stress required to trigger decohesion is typically much higher than that obtained via conventional plasticity analysis. The central question then arises: what mechanism is responsible for elevated crack tip stresses that are large enough to trigger cleavage? It is reasonable to suggest that the answer lies in microstructural features not accounted for in conventional plasticity. Recent studies have focused on dislocations, both their interaction with the crack tip and with one another in the presence of large strain gradients.
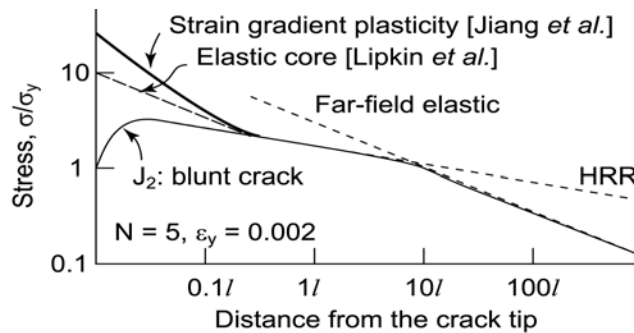

Figure 1: Stress distributions ahead of a crack tip from various modeling approaches and normalized to a material-based length.

3. CRACK TIP STRESS: RECENT ADVANCES

There have been several attempts to rationalize stresses larger than conventional continuum plasticity predictions using dislocation distributions that alter the near tip field. Thompson and Kameda [7] described the stresses adjacent to the tip of an atomistically sharp intergranular crack, invoking a small dislocation-free zone between the crack tip and dislocation pile-up arranged such that it produced a constant tensile stress in the dislocation free zone and joined the HRR field at the outer edge. σ_{YY} in the dislocation free zone equaled $(4\text{-}7)\sigma_Y$ at applied K typical of hydrogen cracking thresholds [7]. Gerberich and coworkers extended this approach by modeling the interaction of a distribution of dislocations that dominate very-near tip stresses and a superdislocation (removed from the tip) that defines global crack tip plasticity with work hardening [8,9]. The near-tip dislocations are arranged to produce a constant frictional sliding stress along the dislocation pile-up, canceling the crack tip singularity and producing a non-monotonic stress field with $\sigma_H \sim (30\text{-}50)\sigma_Y$, maximized 20 nm ahead of a sharp crack tip [10].

These works are distinct from dislocation-free core approaches, which include an "elastic core" that precludes dislocations and results in an elastic stress distribution, with a corresponding crack tip stress intensity factor that is lower than the elastic far field stress intensity factor. Lipkin *et al.* raise the interesting point that if rate of strain hardening exceeds the divergence of the stress field, the material can no longer plastically deform – this occurrence is guaranteed by a large strain gradient which requires geometrically necessary dislocations and increase hardening [11]. The size of the elastic core is determined by stress continuity with the HRR field, opposed to plastic fields controlled by the superdislocation in the models of Gerberich and co-workers. Calculations for similar material properties as used in the J_2 curve place the size of the elastic core at ~250 nm (or 0.$25l$ in Fig. 1). In terms of near tip stresses, significant stress elevation over the J_2 results is predicted over 100-300 nm, as shown in Fig. 1.

The concept of geometrically necessary dislocations provides a related explanation as to why crack tip stresses may be higher than conventional plasticity predictions [12,13]. Geometrically necessary dislocations accommodate large strain gradients, implying that strain hardening is exacerbated at crack tips where gradients are implicit. Rather than explicit reference to individual dislocations, the models rely on an intrinsic material length scale that controls the contribution of strain gradient to Taylor-based strain hardening. This length scale can be taken as a phenomenological constant that relates to microstructure [13] or is connected analytically to specific dislocation interactions [14]. The curve in Fig. 1 depicts the σ_{YY} stress distribution resulting from incorporating strain gradient terms into the hardening description [14]. The length scale of the stress elevation is controlled by the material length scale, l; this parameter has been inferred to be 0.5-5 μm from micro-indentation and wire torsion experiments applied to model single phase metals [13]. For comparison with dislocation-based models, it is convenient to assume $l = 1$ μm. For this case, it is clear that the strain gradients are large enough to significantly alter the HRR fields over ~ 300 nm. Currently, the location of the maximum stress in an SGP-affected fracture is not clear, since only asymptotically sharp cracks have been modeled. Note that the stress elevation predicted by Gerberich et al. for single crystal Fe-Si [10] is considerably greater than that depicted in Fig. 1; however, Fe-Si exhibits very high work hardening, which exacerbates the stress elevation predicted by strain gradient modeling.

The concepts introduced by explicit treatment of near tip dislocations and enhanced hardening due to strain-gradients are supported by discrete dislocation dynamic simulations [15]. This approach incorporates individual dislocations into a single crystal plasticity framework, and tracks movement using dislocation mobility models. The models account for dislocation nucleation, annihilation and interaction with obstacles; the number of dislocations and their equilibrium positions are determined by solving the full boundary value problem coupled to conventional dislocation constitutive descriptions, without a priori assumptions regarding

dislocation arrangement (only the location of sources and obstacles). The possibility of crack advance is incorporated using a cohesive zone model that requires an atomistically-motivated traction-separation relationship, with a maximum cohesive stress and critical separation distance as inputs. The resulting near-tip fields reveal many of the same characteristics obtained via continuum models that invoke a priori assumptions of dislocation behavior [15]: (i) crack tip openings remain sharp, (ii) near tip stresses are significantly higher than those predicted by plasticity models without reference to material microstructure, (iii) a dislocation free zone can arise near the crack tip, and (iv) crack tip shielding (or the relationship between far field applied stress intensity factor and intrinsic toughness) is a strong function of the density of dislocation nucleation sources. Quantitative comparison of maximum stresses at the crack tip with the models discussed above is not feasible due to the inclusion of a cohesive zone with finite critical stress.

5. IMPLICATIONS FOR HYDROGEN ENHANCEMENT NEAR THE CRACK TIP

The presence of large elastic stresses in the sub-micron FPZ is a central requisite for hydrogen embrittlement by decohesion, as first recognized qualitatively by Oriani [16] and affirmed in recent reviews [1,9,17]. The primary reason for this requirement is the need to raise the otherwise low lattice and reversibly trapped solubility of H at crack nucleation sites. Higher concentrations of H justify lowering cohesive strength of the lattice or interface. The concentration of H in interstitial lattice sites, C_l, depends exponentially dependence on hydrostatic stress that dilates the lattice [18,19]. Additionally, H segregates to trap sites, in equilibrium with C_l and proportional to the trap binding energy, E_B for dilute H concentration in reversible traps of low to moderate binding energy ($\sim$<40 kJ/mole) [20]. Such trap sites are typically interfaces and boundaries that constitute a connected path for brittle H-cracking. Additionally, dislocation structure from crack tip deformation is an effective trapping state [21]. The total amount of H accumulated at damage nucleation sites ($C_{H\text{-}FPZ\,trap}$) in the FPZ is approximated by:

$$\left(C_{H-FPZ\,trap}\right) = C_l \exp\left(\frac{E_B + (\sigma_H V_H)}{RT}\right) \tag{1}$$

where V_H is the partial molar volume of H in iron, $\sim$2 cm^3/mol Fe.

Consider the results in Fig. 2 [22]. Pre-dissolved H, concentrated in lattice and reversible trap sites at the 0.5-5 ppm level by weight severely embrittles a modern ultra-high strength steel, AerMet$^\circledR$100.Cracking is along interface microstructure in this martensitic steel, with a binding energy for H of $\sim$40 kJ/mol [23]. The source of this unexpectedly severe IHE is suggested by the comparison in Fig. 2.The hypothesis is that H repartitions from a lower binding energy trap state, in this case nano-scale carbides with a coherent interface and $E_B \sim$12 kJ/mol, to the crack tip and martensitic interfaces, when the stress-interaction energy ($\sigma_H V_H$) > E_B for the source trap. The calculation in Fig. 2 shows that this happens for AerMet$^\circledR$100 (σ_Y = 1760 MPa) when the ratio of σ_H/σ_Y > 3.0. The probability that this repartition of H occurs rises as the difference between E_B and $\sigma_H V_H$ increases - demonstrating that IHE is exacerbated by those factors that increase crack tip stresses.

The combined effects of interface trapping and stress concentration of H in the FPZ are dramatic. For a martensite lath boundary in AerMet$^\circledR$ 100, E_B is 40 kJ/mol and $\sigma_H V_H$ is 9–30 kJ/mol for $\sigma_H \sim$ 4.4-15 GPa . The total H concentration ($C_{H\sigma,T}$) is 6 x 10^6 C_l. The lattice solubility of H in AerMet$^\circledR$100 is unknown, but is 3 x 10^{-4} wppm for Fe. Using this lower estimate of C_l, $C_{H\sigma,T}$ is on the order of 1600 wppm (9 atom pct) at 23°C.
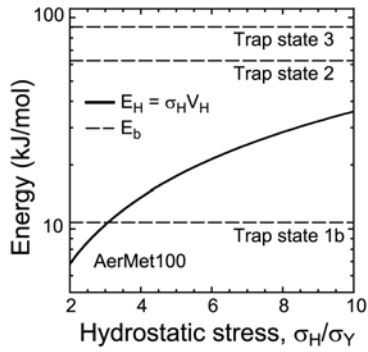
Figure 2: The interaction energy $E_H = \sigma_H V_H$ vs. hydrostatic stress ahead of the crack tip compared with E_b for major trap states in aged ultra-high strength alloy steel.
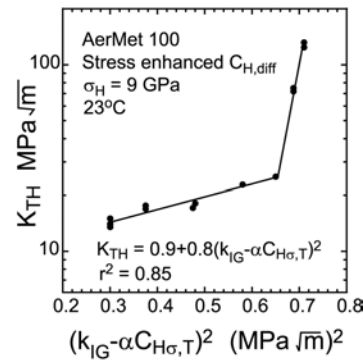
Figure 3: Effects of trap+stress enhanced H concentration $C_{H\sigma,T}$ ozn the threshold for IHE. Measured $K_{TH} < 30$ MPa m$^{1/2}$ relate to brittle, transgranular cracking; cracking at higher K_{TH} involved some micro-void coalesence.

The effect of increasing lattice H concentration in reducing the measured threshold for IHE, K_{TH}, is predicted by coupling this trap and stress enhanced crack tip H content with Gerberich's formulation for crack tip H embrittlement [24]. The comparison of theory and experiment is shown in Fig. 3 [22]. The model predicts:

$$K_{TH} = \frac{1}{\beta'_{IHE}} \exp\left[\frac{\left(k_{IG} - \alpha C_{H\sigma,T}\right)^2}{\alpha'' \sigma_Y} \right] \qquad (2)$$

where k_{IG} is the critical Griffith stress intensity factor for cleavage fracture without H ($G_C \sim \gamma_S \sim k_{IG}^2/E$), and γ_S is the energy required to produce unit crack surface. β' and α'' are constants determined by computer simulation of the dislocation structure about the crack tip. The fit to the IHE data in Fig. 3 yielded values of these adjustable constants essentially equal to those necessary to fit measured K_{TH} vs. surrounding H$_2$ pressure for HEE of a high strength steel [24]. These results suggest that modern formulations of high crack tip stresses are reasonable and necessary for next generation models of hydrogen embrittlement. There are, however, substantial uncertainties in the details of such formulations, as well as in the effect of H on the cohesive zone relationship that must be coupled to predict cracking.

6. CONCLUSIONS

Accurate assessment of crack tip stresses is critical to understanding the effect of hydrogen in embrittlement mechanisms; stress controls hydrogen concentration which lowers cohesive strength and drive separation. Recent crack tip models include material microstructure (be it explicit modeling of near-tip dislocations or inherent material length scales) and predict that crack tip stresses are 2-10 times higher than conventional plasticity predictions. A variety of approaches predict that these elevated stresses occur over 100-300 nm, which is greater than conventional plasticity descriptions. These elevated stresses impact hydrogen concentration, implying that lattice-dissolved H is not negligible compared with trapped H, which in turn predicts significant lowering of threshold stress intensity factor by decohesion.

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