JOURNAL OF MATERIALS SCIENCE 27 (1992) 3203–3205

Theory of hydrogen-assisted crack growth

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A model for hydrogen-induced cracking is proposed and developed on the assumption that hydrogen enters the embrittling process zone (EPZ) ahead of the crack-tip and promotes localized plastic flow which is proportional to its concentration. The formulae of the criterion for crack propagation, K_{IH}, and the crack growth rate dl/dt, are derived and applied to the experimental data of AISI4340 superhigh-strength steels.

1. Introduction

As is well known, the presence of hydrogen at or near the tip of a crack which leads to slow crack growth and delayed fracture in medium- to high-strength materials, remains a controversial subject, although several mechanisms have been proposed to explain this phenomenon on a microscopic level [1–3]. In brief, the microphysical features for hydrogen-induced delayed fracture [4–6] can be described as follows. There is an embrittling process zone (EPZ) at a characteristic distance, d^*, ahead of the crack tips. Hydrogen diffuses to the EPZ under the action of the local chemical–mechanical driving force. When its concentration attains a critical value, hydrogen will aid localized plastic flow, while the dislocation sources begin to activate the production of high-density slip-bands and pile-ups against the microstructure defects in the EPZ, and then to induce secondary cracks. With the propagation of the secondary crack, and coalescence with the main crack, the main crack advance finally occurs. Here the characteristic length, d^*, reflects the sensitive degree of materials microproperties to hydrogen, and is a very important geometric parameter which can be determined by the microstructure of the materials.

The above physical features are peculiar to the crack-tip environment in the process of hydrogen embrittlement fracture; one aspect reveals the micromechanisms of fracture, while also sketching detailed physical pictures for hydrogen accelerating the delayed plastic deformation, which results in the slip-band cracks. It is a typical fracture in which the microcracks nucleate, grow and coalesce with the main crack due to dislocation pile-ups caused by local plastic flow against the microstructure defects within the EPZ ahead of the crack-tip. In this paper the crack propagation mechanisms is discussed quantitatively for an external hydrogen environment.

2. Hydrogen-induced cracking model and the conditions for microcrack nucleation

Based on the above analyses, a cracking model can be proposed in which hydrogen induces the activation of dislocation sources and then produces delayed plastic deformation resulting in slip-bands microcrack initiation within the EPZ. In this model, the most fundamental embrittling mechanism is assumed to be hydrogen weakening the cohesive force between metal atoms, but the cracking mechanism, which induces microcrack nucleation, is slip-band cracking caused by the delayed plastic deformation.

To express the conditions for microcrack nucleation with respect to the above cracking models, we have

$$C_H(t) = C_H^* \qquad (1)$$

$$\sigma_f \geqslant \sigma_f^* \qquad (\text{equality at } x = d^*) \qquad (2)$$

where Equation 1 indicates that the local concentration of hydrogen must attain a critical value within the EPZ, and Equation 2 shows the local stress must reach or exceed the critical stress. The calculation of σ_f^* depends on the cracking mode of slip-bands. To evaluate existing experimental data [7, 8], the pile-up models of Zener–Stroh, Cottrell, and the equivalent Griffith crack dislocation array may be selected as the dislocation models of slip-band cracking proposed in this paper. Thus, calculation of σ_f^* is very easy.

A rigorous calculation of the hydrogen concentration may be a difficult task, due to the evolution of the EPZ and the mathematical difficulties in obtaining analytical transient solutions of the relevant stress-assisted diffusion equation. To obtain the critical concentration of hydrogen, C_H^*, we can construct a deformation potential model for the diffusion of hydrogen to crack-tip regions which can be found in the papers of McMullen *et al.* [9]. The hydrogen diffusion equation is given by Fick's law as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \frac{D}{kT}\frac{\partial}{\partial x}\left(C\frac{\partial V}{\partial x}\right) \tag{3}$$

where D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, and

$$V = \frac{2}{3}E_{\mathrm{d}}\beta\left(\frac{M}{x}\right)^q \tag{4}$$

is the deformation potential which gives a driving force for hydrogen diffusion to the EPZ, and the physical meanings resulting from the gradient of the dilation field. E_{d} is the deformation potentials for hydrogen in metals, q is the singularity order of the strain field, M is the control parameter of the crack-tip strain field, and β is an experimental constant. In the highly plastic extended zone,

$$M = \delta_{\mathrm{t}}(\mathrm{COD}) = \frac{K_{\mathrm{I}}^2}{2\sigma_{\mathrm{ys}}E} \tag{5}$$

and

$$q = 1 \tag{6}$$

where K_{I} is the Mode I stress intensity factor, σ_{ys} is the yield stress, E is Young's modulus, and COD is the crack opening displacement.

Solving Equations 3–6 simultaneously,

$$C_{\mathrm{H}}(t) \simeq \frac{C_0 D}{(a - d^*)d^*}t\exp\left[\frac{E_{\mathrm{d}}\beta}{6kTd^*}\left(\frac{K_{\mathrm{I}}^2}{\sigma_{\mathrm{ys}}E}\right)\right] \tag{7}$$

where C_0 is the concentration of hydrogen in the absence of external stress, $(a - d^*)$ is the EPZ size. At the critical stage, because $t = t_{\mathrm{n}}$, the incubation time required to form a microcrack, we have

$$C_{\mathrm{H}}^* = \frac{C_0 D}{(a - d^*)d^*}t_{\mathrm{n}}\exp\left[\frac{E_{\mathrm{d}}\beta}{6kTd^*}\left(\frac{K_{\mathrm{I}}^2}{\sigma_{\mathrm{ys}}E}\right)\right] \tag{8}$$

3. Criterion for hydrogen-induced crack propagation: calculation of K_{IH}

In view of the arguments presented in the previous sections, if and only if, the plastic flow induced by hydrogen within the EPZ reaches a critical state, the secondary crack initiates and the main crack propagates. Accordingly, we can simplify the calculation of K_{IH} as in Fig. 1, and the physical meanings can be explained as the n dislocations which can be viewed as a large dislocation for $d^* \gg nb$ at $x = d^*$ ahead of the main crack, interacting with the main crack which results in propagation of the crack. According to existing experimental information, we know that dislocation densities (***nb***) (***b*** is the Burgers vector) is proportional to the concentration value of hydrogen C_{H}. Without loss of generality, it is always possible to postulate that

$$nb = \alpha C_{\mathrm{H}} \tag{9}$$

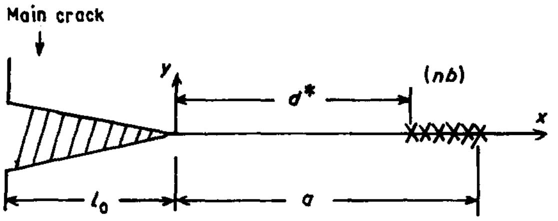

Figure 1 Schematic representation of the EPZ and the crack-dislocations interaction model for calculating threshold stress intensity in hydrogenous environment.

where α is a dimensional constant.

To calculate the stress intensity factor at a microscopic level, we have the formulae [10]

$$\begin{cases} K_{\mathrm{I}}^2 = 2\pi^3 A^2 \lim\limits_{x\to 0}(-x)f^2(x) \\ A = \dfrac{\mu b}{2\pi(1-\nu)} \end{cases} \tag{10}$$

where $f(x)$ is the dislocation densities of the crack body which can be calculated as follows

$$\int_{-l}^{0}\frac{\mu b}{2\pi(1-\nu)}\frac{f(x)\,\mathrm{d}x}{(d^* - x)} + \frac{\mu nb}{2\pi(1-\nu)}\frac{1}{d^*} + \sigma = 0 \tag{11}$$

where l is the crack length. Inserting Equations 9 and 11 into Equation 10

$$K_{\mathrm{I}} = \sigma(2\pi l)^{1/2} - \frac{\mu(2\pi l)^{1/2}}{2\pi(1-\nu)}\frac{\alpha C_{\mathrm{H}}}{[d^*(l + d^*)]^{1/2}} \tag{12}$$

In the absence of hydrogen, i.e. $C_{\mathrm{H}} = 0$, $K_{\mathrm{I}} = K_{\mathrm{IC}}$, the fracture toughness which corresponds to the initiation of unstable crack propagation; here

$$\begin{cases} K_{\mathrm{IC}} = \sigma(2\pi l_{\mathrm{c}})^{1/2} \\ l_{\mathrm{c}} = \dfrac{G_{\mathrm{IC}}E}{\pi(1-\nu^2)\sigma}\ \text{(the critical crack length)} \end{cases} \tag{13}$$

In the presence of hydrogen, once $C_{\mathrm{H}} = C_{\mathrm{H}}^*$, this corresponds to $K_{\mathrm{I}} = K_{\mathrm{IH}}$, the threshold stress intensity factor, then the crack begins to propagate. Accordingly

$$K_{\mathrm{IC}} - K_{\mathrm{IH}} = \frac{\mu(2\pi l_{\mathrm{c}})^{1/2}}{2\pi(1-\nu)}\left\{\frac{\alpha C_{\mathrm{H}}^*}{[d^*(l_{\mathrm{c}} + d^*)]^{1/2}}\right\} \tag{14}$$

This is the fundamental equation to determine K_{IH} which is based on the new proposed cracking models.

4. Rate of hydrogen-induced crack propagation: calculation of $(\mathrm{d}l/\mathrm{d}t)$

When $K_{\mathrm{I}} > K_{\mathrm{IH}}$, the crack grows into a steady stage. We confine our discussion to the case for the diffusion of dissolved hydrogen to the EPZ is a control process, hence the general expression for crack growth rate can be written as

$$\frac{\mathrm{d}l}{\mathrm{d}t} = \frac{d^*}{t_{\mathrm{n}}} \tag{15}$$

where d^* and t_{n} are as before. Substituting Equation 8 into Equation 15, we have

$$\frac{\mathrm{d}l}{\mathrm{d}t} = \left(\frac{D}{a - d^*}\right)\left(\frac{C_0}{C_{\mathrm{H}}^*}\right)\exp\left[\frac{E_{\mathrm{d}}\beta}{6kTd^*}\left(\frac{K_{\mathrm{I}}^2}{\sigma_{\mathrm{ys}}E}\right)\right] \tag{16}$$

5. Discussion

To discuss the influence of hydrogen environment pressure, P, on the threshold stress intensity factor, K_{IH}, we can substitute Equation 8 into Equation 14. According to Sieverts' law, $C_0 = SP^{1/2}$, where S is the Sieverts constant for a metal lattice. Hence

$$\ln\left[\frac{P}{(K_{\mathrm{IC}} - K_{\mathrm{IH}})^2}\right] = A_0 - A_1 K_{\mathrm{IH}}^2 \qquad (17)$$

$$A_0 = 2\ln\left\{\frac{2\pi(1-\nu)}{\mu(2\pi l_c)^{1/2}}\frac{(a-d^*)d^*}{Dt_n\alpha S}\left[d^*(l_c + d^*)\right]\right\} \qquad (18a)$$

$$A_1 = \frac{E_d\beta}{3kTd^*\sigma_{ys}E} \qquad (18b)$$

Equation 17 indicates that K_{IH} will decrease as the pressure, P, increases. This conclusion is good qualitative agreement with the experimental observation. It is also interesting to notice that Equation 17 is the first fundamental relationship between P and K_{IH} derived from the idea of hydrogen accelerating local plastic flow.

For a quantitative, calculation we can select the experimental data for AISI4340 superhigh-strength steel ($\sigma_{ys} = 1720$ MPa, $K_{\mathrm{IC}} = 66$ MPa m$^{1/2}$) [11]. It is obvious that the $K_{\mathrm{IH}} \sim P$ relationships (Equation 17) will fit completely to the experimental curves if we take $A_0 = -6.9757$, $A_1 = 0.0129$, as in Fig. 2. In the meantime, we can also obtain $d^* = 5.89$ μm, $\alpha = 3.48$. (For this calculation, the respective parameters are assumed to be $t = 100$ s, $E = -2.01$ eV, $\beta = 1$, $S = 1.26 \times 10^{-8}$(H)/(Fe) (torr)$^{-1/2}$, $a = 10$ μm, $D = 1.23 \times 10^{-10}$ m^2 s^{-1}.) This calculated value of d^* is in excellent agreement with the existing experiments [12]. During the calculation, the unknown parameters emerging in our discussion can either be measured experimentally or be calculated theoretically. Using the new model, we can calculate not only the concentration of hydrogen but also the number densities for activated dislocations.

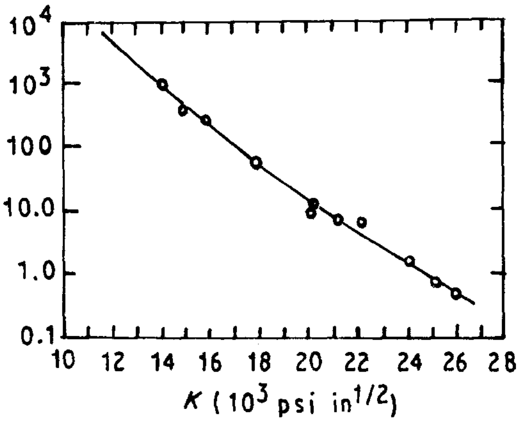

Figure 2 Effect of H_2 pressure on threshold stress intensity K_{IH}: Experimental data (circles) [11] and regression analysis fit (solid line) of Equation 17. (Torr × 133 = Pa; ksi$\sqrt{\text{in}}$ × 1.10 = MNm$^{-3/2}$).

Accordng to Equation 11, the value of (dl/dt) will tend to infinity for $a \rightarrow d^*$ or for $d^* \rightarrow 0$. The former corresponds to the EPZ size, $(a - d^*)$ tending to zero, which indicates that fracture takes place almost without the action of hydrogen, and the latter corresponds to no EPZ existing, which indicates that the crack will propagate unstably. Both cases indicate that the material approaches fracture toughness, K_{IC}, thus, we have (dl/dt) tending to infinity. This also indicates that the rate formula (Equation 16) corresponds to the stage of $K_{\mathrm{IH}} \leqslant K_{\mathrm{I}} < K_{\mathrm{IC}}$.

Comparing with the existing theoretical models, this theory emphasizes the particular function of EPZ in the process of crack propagation. The location for EPZ is always at a site where the local hydrostatic stress is maximum. It is thought that the macro incontinuity at trap sites near the location of the stress maximum, solely nucleates the microcrack, and the combined action of hydrogen concentration and local plastic flow result in the secondary crack initiation. The EPZ is not a point, but a body in which there are large microstructural defects.

6. Conclusions

1. It is proposed that the delayed cracking process resulting from hydrogen damage is the united action of both hydrogen inducing a lattice embrittlement thus weakening the cohesive force between metal atoms, and hydrogen accelerating the local plastic flow. The process for hydrogen-induced delayed fracture is viewed as a process driven by plastic flow, but not a cleavage. Accordingly, a micromechanism for hydrogen embrittlement has been developed.

2. The theoretical formulae for K_{IH} and crack growth rate have been derived from the new proposed model. All the results are universal and agree with the experimental data of Oriani and Josephic [11].

Acknowledgement

This work was supported by the National Natural Science Foundation of China.

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Received 22 November 1990
and accepted 10 April 1991

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*1 torr = 19.2903×10^{-3} psi
1 torr = 1.33×10^2 Pa
1 psi = 6.8946×10^3 Pa