A STUDY ON TRANSPORT OF HYDROGEN ATOMS AROUND
A CRACK TIP AND THE DECOHESION MODEL

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INTRODUCTION

The mechanism of hydrogen transport in materials is one of important
topics in the study of hydrogen embrittlement, especially in the study of
hydrogen-assisted subcritical crack growth. However, the mechanisms of
hydrogen transport and embrittlement are still not clarified at present.
In the study of hydrogen transport near a crack tip, previous authors
adopted macroscopic stress fields with either singular behavior or some
kind of plastic zone correction at the crack tip[1-3]. This study adopts
microscopic stress fields calculated by Schmidt and Woltersdorf who took
into account the effect of cohesive stress and the proposed results might
be valid in the region very near the crack tip[4]. It is also assumed
that the presence of a hydrogen atom in a bcc unit cell will cause tet-
ragonal distortion of the unit cell and the stresses around the crack tip
will introduce an attractive force on hydrogen atoms. Thus hydrogen atoms
can diffuse from the clean crack surfaces to the region ahead of the tip,
and reduce strain energy and cohesive strength thereby. This concept
actually is a combination of "Cottrell atmosphere"[5] and the decohesion
model of hydrogen embrittlement[6]. Based on the above concept, a transport
model of hydrogen atoms around the crack tip is proposed in this paper.
The flow patterns of hydrogen atoms, the average saturated hydrogen con-
centration at the crack tip and the decrease of cohesive strength are
presented. Finally, the discussion will be on the possible fracture plane
of the cracking and on the extension of the model to the case of inter-
granular cracking.

THE MODEL

To simplify the model, consider a plane crack with the tip inside a grain. The size of the grain is assumed to be at least one order larger than that of cohesive zone. Let δ be the distance between the neighbouring crystal planes which have formed and will form crack surfaces. Let the origin of coordinate system be at the crack tip which is just at the midpoint of δ_m, and assume the nearest position of the unit cell is at $(\delta_m/2, \pi/2)$. Fig. 1 shows the position of an arbitrary unit cell with the (100)-axis making an angle of ϕ with respect to the x-axis.
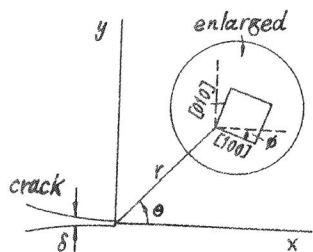

Fig. 1 An arbitrary unit cell near the crack tip

Let ε_1, ε_2 and ε_3 be the principal strains in the (100)-, (010)- and (001)-directions, respectively, of the tetragonally distorted cubic unit cell containing one hydrogen atom. The strain components in the xyz-system are given by

$$\varepsilon_x^H = \varepsilon_1\cos^2\phi + \varepsilon_2\sin^2\phi , \qquad \varepsilon_y^H = \varepsilon_1\sin^2\phi + \varepsilon_2\cos^2\phi$$

$$\varepsilon_{xy}^H = (\varepsilon_1 - \varepsilon_2)\cos\phi\sin\phi, \qquad \varepsilon_z^H = \varepsilon_3 \qquad (1a)-(1d)$$

Microscopic stresses at the point (r, θ) near the tip of a mode I crack are given by (4)

$$\sigma_x^C = Ar^{-n}[\cos n\theta - n\sin\theta \, \sin(n+1)\theta]$$

$$\sigma_y^C = Ar^{-n}[\cos n\theta + n\sin\theta \, \sin(n+1)\theta]$$

$$\sigma_{xy}^C = Ar^{-n} \, n\sin\theta \, \cos(n+1)\theta$$

$$\sigma_z^C = (\sigma_x^C + \sigma_y^C), \quad \text{plane strain case} \qquad (2a)-(2d)$$

where ν is Poisson ratio and n is determined by the shape of crack surfaces with value between 0 and 1; when $n = \frac{1}{2}$, eqs. (2a) to (2c) recover

the functional forms of linear elastic results. A is determined by $\sigma_y^C(\delta_m/2, \pi/2) = \sigma_m$, where σ_m is the cohesive strength in absence of hydrogen atoms.

$$A = \sigma_m(\delta_m/2)/[\cos(n\pi/2) + \sin(n\pi/2 + \pi/2)] \qquad (3)$$

Following the literature [7], the interaction energy per unit cell is given by

$$U_{int} = -\sum_{i,j=x,y,z} \sigma_{ij}^C \varepsilon_{ij}^H \qquad (4)$$

As an example, in the following only results obtained at $n=\frac{1}{2}$, ε_1=const., and $\varepsilon_2 = \varepsilon_3 = 0$ are presented.

(1) Flow Patterns of Hydrogen Atoms

By letting U_{int} equal to different constant values, we can construct a system of equipotential lines with flow lines orthogonal to them. From Einstein's formula of drift flow, we can show that the flow directions always finally point toward the small region ahead of the crack tip. The flow patterns with crack surfaces on the (100)-plane $(\phi=\frac{1}{2}\pi)$ and on the (110)-plane $(\phi=\frac{1}{4}\pi)$ are shown in Fig. 2a and Fig. 2b respectively.
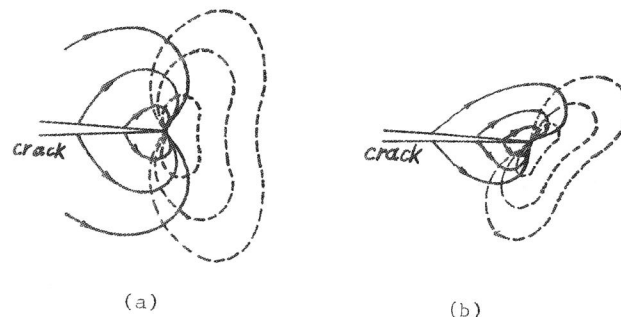

(a)   (b)

Fig. 2 Flow patterns with crack surfaces on (a) the (100)-plane and (b) the (110)-plane.

(2) Saturated Hydrogen Concentration at the Crack Tip

With the presence of hydrogen atoms, the strain component is reduced to

$$\varepsilon_{ij} = \varepsilon_{ij}^C - \rho \varepsilon_{ij}^H, \quad i,j = x,y,z \tag{5}$$

where ε_{ij}^C can be determined from eqs. (2a)–(2d) and the strain-stress relation, ρ is average number of hydrogen atom in a cubic unit cell. The strain energy density can be obtained by using eq. (5) and the formula of strain energy density in elasticity. The number of hydrogen atoms that can diffuse to the crack tip is limited because, at saturated concentration, additional segregation no longer reduces the strain energy in the region near the crack tip. Thus the saturated concentration can be obtained when the strain energy reaches a minimum value at the tip. The average saturated concentration at the nearest unit cell is given by

$$\rho_m = \frac{16(1+\nu)(1-2\nu)(2+\sin^2\phi)}{15\sqrt{2\pi}\ (1-\nu)\varepsilon_1} \left(\frac{\sigma_m}{E}\right) \tag{6}$$

where E is elastic modulus. It is resonable to assume that $\varepsilon_1 = 0.2$, $\nu = 0.3$ and $\sigma_m/E = 0.1$, then ρ_m will be less than 0.27 but larger than 0.18 for irons and steels.

(3) Decrease of Cohesive Strength

Cohesive strength with the presence of hydrogen atoms is given by $\sigma_m(H) = \sigma_y(\delta_m/2, \pi/2)$, where σ_y can be obtained from the stress-strain relation and eq. (5). At the saturated concentration ρ_m, the decrease of the cohesive strength is given by eq. (7).

$$1 - \frac{\sigma_m(H)}{\sigma_m} = \frac{8\sqrt{2}}{15\pi} \left(\frac{\nu}{1-\nu} + \frac{1-2\nu}{1-\nu}\sin^2\phi\right)(2+\sin^2\phi) \tag{7}$$

From eqs. (6) and (7), it can be seen that at $\phi = \frac{1}{2}\pi$, the decrease of the cohesive strength reaches a maximum and the ρ_m also reaches a maximum. If taking $\nu = 0.3$ and $\phi = \frac{1}{2}\pi$, the value of $1 - \sigma_m(H)/\sigma_m$ will be about 72%, this means that the cohesive strength at the maximum hydrogen concentration will reduce to 0.28 of that at the absence of hydrogen atoms.

DISCUSSION AND CONCLUSION

If cubic unit cells in a grain are extended in the direction of the (100) - axis and the crack surfaces are on the (100) - cleavage plane, then average hydrogen concentration in the small region ahead of the crack tip can reach the maximum value and so does the amount of decrease of the cohesive strength. This suggests that the possible fracture surfaces will remain on the (100)—cleavage planes, and the Oriani's decohesion model (6) is suitable to explain the mechanism of hydrogen-induced cracking. Although the mechanism of hydrogen transport may be different, this prediction is consistent with the results of hydrogen charging experiments for alpha-iron and 3% Si iron[8,9]. For hydrogen-assisted subcritical crack growth in martensitic high strength steels, because only the clean crack surfaces very near the tip, through the chemical surface reaction, can supply hydrogen atoms to the very small region ahead of the tip, the selection of microscopic stress fields seems quite reasonable. Besides, the diffusion due to hydrogen concentration gradient in the media is slow, which gives the distance of the hydrogen transport in a time interval at least one order less than the increment of the rate-controlling crack growth during the same time interval for an AISI 4340 steel in 20 torr H_2S[10]. Thus the transport of hydrogen atoms in the media is more likely due to the drift flow, at least at the initial stage, which is caused by the interaction between the stresses around the tip and the distortion of the cells in the presence of hydrogen atoms. However, hydrogen-assisted subcritical crack growth in high strength steels usually yields intergranular separation along prior-austenitic grain boundaries and some limited amount of quasi-cleavage feature. In this case, the grain boundary ahead of the crack tip may be idealized as a strip with the width of δ. After neglecting the difference between the orientations of cubic unit cells separated by the grain boundary, the flow model proposed by this paper can still be applied qualitatively, and the decohesion model can be used to describe the mechanism of hydrogen-assisted crack growth.

This paper has presented the drift flow model for hydrogen atoms around the crack tip. Based on the decohesion model, the estimations of the average saturated hydrogen concentration and the decrease of the cohesive strength have been made. The model provides an unified concept among the transport of hydrogen atoms, the possible maximum concentration at the crack tip, the decrease of the cohesive strength, and the cracking mechanism. It appears that this model can be quantitatively or qualitatively applied to hydrogen-induced cracking in some bcc irons and martensitic high strength steels.

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