

A Preliminary Model for Crack-tip Hydrogen Transport

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ABSTRACT

A preliminary analysis has been made of the hydrogen concentration distribution at the tip of a crack as a basis for a more rigorous model leading to prediction of crack growth kinetics. The distinctive features are the use of a boundary fitted coordinate method for the numerical analysis and the adoption of flux boundary conditions at the crack tip and crack walls. At this stage of development simple analytical expressions for the stress state have been employed. Using limiting cases, the boundary fitted coordinate method has been shown to give results comparable with boundary integral and finite element methods. Comparison of predictions of the hydrogen distribution at the crack tip from constant concentration and flux boundary conditions indicates that the latter should be adopted for application to low alloy steels, but equivalent results can be obtained for face centred cubic lattices because of the much lower lattice diffusivity.

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1 INTRODUCTION

Hydrogen assisted cracking is an important failure process for a range of metals in aqueous environments and considerable effort has been made to predict threshold stress intensity factors for cracking and crack growth rates¹⁻¹⁸. However, the models used have often been of limited applicability because of the complexity of factors which must be considered for reliable prediction. In particular, models of cracking have to account for the electrochemical kinetics of hydrogen atom generation, the absorption of the hydrogen atoms, transport and localisation in the metals and the interaction of the hydrogen atoms with the material under conditions of localised stress and strain. In essence, prediction of behaviour depends on quantifying the time-dependent distribution of hydrogen atoms in the crack tip region as a function of environmental and mechanical parameters, and the response of the material to the localised hydrogen content in the form of crack advance.

At the present time, the relationship between the mechanism of the damage process and the extent of crack advance is poorly developed in quantitative terms and modelling is based usually on a requirement to achieve certain combined levels of hydrogen concentration and stress or strain over a critical microstructural distance. The relevant parameters are usually derived empirically from measured crack growth rates or thresholds.

There have been a number of studies aimed at predicting the hydrogen concentration at crack tips with varying levels of complexity. The models differ in relation to the dimensionality of the problem, the stress distribution and the inclusion of hydrogen trapping. The early models took account of localisation of hydrogen concentration associated with lowering of the chemical potential in the region of high hydrostatic stress at the crack tip¹⁹. The definition of the hydrostatic stress (σ_{kk}) was based initially on an elastic solution with

$$\sigma_{kk} = \frac{2(1+\nu_p)}{3(2\pi r)^{1/2}} K_I \cos\left(\frac{\theta}{2}\right)$$

where K_I is the mode I stress intensity factor, ν_p is Poisson's ratio and r and θ are radial co-ordinates. (The definition of all the symbols to be used in this report is given in Appendix 1). Subsequent analysis²⁰ included plasticity at the crack tip with σ_{kk} in the plastic zone given by

$$\sigma_{kk} = \frac{2(1+\nu_p)}{3(2\pi r_p)^{1/2}} K_I \cos\left(\frac{\theta}{2}\right)$$

where r_p is the size of the plastic zone.

Unger and Aifantis²¹ used a one-dimensional treatment with σ_{kk} constant in the plastic zone and given by

$$\sigma_{kk} = \frac{2}{3} (1 + \nu_p) \sigma_y$$

where σ_y is the yield strength. The elastic solution was used outside the plastic zone. They also considered an alternative stress distribution in the plastic zone at the crack tip based on slip line theory,

$$\sigma_{kk} = \sigma_y [0.5 + \ln(1 + x/\rho_c)] \quad (1.4)$$

where ρ_c is the crack tip radius. In this case, the hydrostatic stress increases from the crack tip to the edge of the plastic zone.

The feature of these early models from a computational perspective was the relative simple analytical solutions for the stress distribution. More complex numerical schemes were developed by Kitagawa and Kojima²² to incorporate a stress distribution calculated based on elastic - perfectly plastic material. For their analysis the stress tended to infinity at the crack tip necessitating some truncation, although the details were not given. An important feature of this work was the consideration of hydrogen trapping using the basic approach first established by McNabb and Foster²³. However, the number of traps was assumed to depend on the hydrostatic stress rather than on the localised strain and this seems unrealistic.

Sofronis and McMeeking^{24,25} used a more rigorous analysis for the distribution of stress and strain at the crack tip based on elastic-plastic theory for a blunted crack-tip. Their model also took account of trapping although they gave emphasis to trapping at low occupancy. The trapping was assumed to be associated primarily with dislocations with a spatially dependent density related to the strain distribution.

More recently, Gerberich and Foeche²⁶ have predicted crack tip hydrogen content based on a discretised dislocation model utilising anisotropic elasticity. In this model, based on experimental studies of hydrogen cracking of Fe-Si single crystals, the crack tip is assumed to be relatively sharp due to the effect of hydrogen on crack-tip angle. However, the extent to which this is applicable to other alloys remains to be clarified. It should be emphasised that none of the models take account of the effect of the varying concentration of hydrogen atoms ahead of the crack tip on crack tip plasticity. This decoupling of the stress distribution and hydrogen distribution enormously simplifies the problem and is justified to an extent in view of the uncertainty in the magnitude of the effect of hydrogen on plasticity, as discussed by Turnbull¹⁸.

A more important limitation of the various models concerns the boundary conditions which are based on the assumption of a constant value of the subsurface concentration, or on a zero value for the flux. The most obvious example where this assumption can become invalid concerns the analysis of previously charged specimens or samples undergoing simultaneous bulk charging as in cathodic polarisation of low alloy steels in sea water. Depending on the charging conditions there may be a net flux of hydrogen atoms out of the crack tip²⁷.

The objective of this study is to develop a model for the hydrogen atom distribution at the crack tip which incorporates flux boundary conditions. In view of the overall complexity of the problem the model is being developed in stages. The first stage of the work incorporates flux boundary conditions and reversible and irreversible trapping with simple analytic solutions for the stress distribution. The second stage will extend this model to more realistic stress and strain conditions based on elastic-plastic theory for a blunted crack tip.

This report describes the development of the model and the numerical technique for the first stage and gives illustrative examples of the results. A distinctive feature of the numerical approach is the application of the boundary fitted co-ordinate method in contrast to the more conventional finite element method.

2 MATHEMATICAL MODEL

2.1 DESCRIPTION OF THE MASS CONSERVATION EQUATIONS

The mass conservation of lattice hydrogen (C), reversibly trapped hydrogen (C_r) and irreversibly trapped hydrogen (C_i) is described by

$$\frac{\partial C}{\partial t} = D \nabla^2 C + \nabla \left(- \frac{DC}{R_g T} \cdot \bar{V}_H \nabla \sigma_{kk} - \frac{\partial C_r}{\partial t} - \frac{\partial C_i}{\partial t} \right)$$

$$\frac{\partial C_r}{\partial t} = N_r(t) \frac{\partial \theta_r}{\partial t} + \theta_r(t) \frac{\partial N_r}{\partial t}$$

$$\frac{\partial C_i}{\partial t} = N_i(t) \frac{\partial \theta_i}{\partial t} + \theta_i(t) \frac{\partial N_i}{\partial t}$$

and

$$\frac{\partial \theta_r}{\partial t} = k_r C (1 - \theta_r) - p_r \theta_r - \frac{\theta_r}{N_r} \frac{\partial N_r}{\partial t}$$

$$\frac{\partial \theta_i}{\partial t} = k_i C (1 - \theta_i) - \frac{\theta_i}{N_i} \frac{\partial N_i}{\partial t}$$

Here $\bar{V}_H$ is the partial molar volume of hydrogen atoms, D is the lattice diffusion coefficient, R_g is the gas constant, T is the absolute temperature, θ_r and θ_i are the fractional occupancy of reversible and irreversible trap sites respectively and $N_r(t)$ and $N_i(t)$ are respectively the density of reversible and irreversible trap sites and may be functions of position and time. The dependency of N_r and N_i on time arises if new sites are being created because of plastic deformation processes or because of growth of voids, and the dependency on position relates to the variation in degree of deformation and stress with distance from the notch or crack tip. For this first stage of modelling $\partial N / \partial t$ has been assumed to be zero.

The geometry of the system adopted is shown in Figure 1a. For reasons of symmetry only half of the total region need be considered. The region of interest is bounded by AEDCBA with the crack walls described by DE (= l) and the crack tip radius by a. AB is the line of symmetry. In the diagram Cartesian axes are shown with origin at O. For convenience, the crack is assumed to be parallel-sided but this can be modified to allow for variable crack opening. The choice of geometry of the crack tip can also be readily chosen but for this analysis a circular crack tip shape has been adopted. The most important feature is the assumption of a two-dimensional crack. Thus, by definition, there is no net transport in the through-thickness direction. In that context, simultaneous bulk charging through the crack sides cannot be dealt with in a time-dependent fashion (this would require modelling in three dimensions) but the steady-state solution will be valid and the effect of precharging can be considered.

It is necessary to define the initial conditions and conditions existing at the boundaries of the system.

Initial conditions:

$$C = C_r = C_i = 0 \text{ for all } x, y \text{ at } t = 0 \quad (2.6)$$

The initial condition can be modified to account for precharging (in the absence of stress) as required.

Boundary conditions

$$C = C_b \text{ on } r = r_b \quad (2.7)$$

$$C = C_b \text{ on } x = -l \quad (2.8)$$

where C_b is a variable input parameter

On the crack wall (DE)

$$J_w = -\frac{D\partial C_w}{\partial y} + \frac{D\bar{V}_H}{R_g T} C_w \frac{\partial \sigma_{kk}}{\partial y} = k_1 \left[\exp \left(\frac{\bar{V}_H}{R_g T} \sigma_{kk} \right) \right] \theta_w - k_{-1} C_w \quad (2.9)$$

$$k_w (1 - \theta_w) - k_w^* \theta_w^2$$

On the crack tip (EA)

$$J_t = -\frac{D\partial C_t}{\partial n} + \frac{D\bar{V}_H}{R_g T} C_t \frac{\partial \sigma_{kk}}{\partial n} = k_2 \left[\frac{\bar{V}_H}{R_g T} \sigma_{kk} \right] \theta_t - k_{-2} C_t \quad (2.10)$$

$$k_t (1 - \theta_t) - k_t^* \theta_t^2$$

θ_w and θ_t are the surface coverages of hydrogen atoms on the crack walls and crack tip respectively; k_1 and k_{-1} are the absorption and desorption rate constants for the crack walls and k_2 and k_{-2} are those for the crack tip.

The stress term $\exp[\bar{V}_H \sigma_{kk}/R_g T]$ multiplying the absorption rate constant arises because of the need to satisfy the condition of increased solubility (lower chemical potential) due to hydrostatic stress. The effect of this stress can be perceived either as a decrease in the activation energy for absorption or a decrease in the potential well of the absorbed hydrogen (increased activation energy for desorption) or a combination of both. In practice, since the absorption and desorption kinetics appear later only as a ratio it is not critical how the stress term is introduced and for convenience it is represented here as decreasing the activation energy for absorption.

The term $k_w(1-\theta_w)$ describes the electrode reaction kinetics for hydrogen or water discharge, which are more familiarly written in the form

$$k_w = \frac{k}{F} C_{H^+}^m (1-\theta) \exp \left\{ -\frac{\beta FE}{R_g T} \right\} \quad (2.11)$$

where C_{H^+} is the hydrogen ion concentration, β is the transfer coefficient, F is Faraday's constant, and E is the electrode potential.

The terms of the form $k_w^* \theta_w^2$ describe the hydrogen atom recombination kinetics. The solution chemistry in the crack is assumed to be at steady state and since the electrode potential does not show marked variation with distance from the crack tip for many systems until near the crack mouth the value of E may be taken to be a constant in the region of interest. Some perturbation of the electrode potential is feasible if the outflow of hydrogen atoms becomes very large but this effect will be neglected. Thus, to a reasonable approximation, the parameter k_w may be considered to be a constant for a particular set of conditions.

Defining conditions at the crack tip is less straightforward because mechanical straining will disrupt crack tip films giving transient kinetics. At this stage of model development the time-averaged parameters will be used and k_t will be defined accordingly. The parameters k_w^* and k_t^* can be derived in principle using the approach described by Iyer and Pickering²⁸ and detailed in Appendix 2. In practice, measurement of the crack-tip value is not readily possible and the assumption is made in application of the model that k_t^* is equivalent to k_w^* .

The parameters k_{abs} and k_{des} are less accessible experimentally. However, for modelling purposes a useful approximation is to assume that they are sufficiently large to ensure equilibrium at the interface for most of the timescale of relevance. This is the basis of the constant C_o value assumed in many hydrogen permeation studies but is a source of confusion in understanding surface controlled transport and diffusion controlled transport of hydrogen atoms. To clarify this issue, equation (2.10) can be written as

$$\frac{J_t}{k_2} = \exp \left(\frac{\bar{V}_H}{R_g T} \sigma_{kk} \right) \theta_t - \frac{k_{-2}}{k_2} C_t \quad (2.12)$$

Clearly, if the term on the left hand side tends to zero then

$$C_t = \frac{k_2}{k_{-2}} \left[\exp \left(\frac{\bar{V}_H}{R_g T} \sigma_{kk} \right) \theta_t \right] \quad (2.13a)$$

which is a constant if θ_t is maintained constant. The validity of this relationship depends on the value of k_2 but importantly also on the magnitude of the flux which will vary as time progresses. Hence, it is possible to reduce the flux equations to a constant concentration boundary condition by choosing appropriate values of k_2 and k_{-2} but this also depends on θ_t remaining constant. In practice, if the specimen is precharged to a high C_o value compared to that expected to be generated by crack tip reactions then the net effect would be that θ_t would alter and C_t would change. The effect of the large value of k_2 would be to maintain equilibrium between surface adsorbed and sub-surface absorbed states but the value of C_t would vary with time. This is quite distinct from the assumption of a constant value

of C_t at the tip, though when there is no precharging or when C_b is small the two approaches converge.

The value of θ_t (and θ_w) can change also for reasons not associated directly with the extent of precharging. The magnitude will depend on the rate of production of hydrogen atoms associated with the discharge reaction and the rate of removal of adsorbed atoms by recombination (to give molecular hydrogen) or by transport into the metal. If the individual rates of discharge and recombination are very large compared with the flux of hydrogen atoms into the metal then the value of θ_t can be considered to be approximately constant, following the approach described in equations (2.12) and (2.13). However, if the flux is large the value of θ_t would change.

Hence, analysis of crack tip hydrogen concentration must incorporate flux boundary equations which include absorption and desorption kinetics and discharge and recombination kinetics. It is important to emphasise that the assumption of flux boundary conditions does not represent the assumption of a constant flux.

No account has been taken of surface diffusion of hydrogen atoms which conceivably could result in transfer of absorbed hydrogen atoms from the crack tip to the crack walls. Incorporation of this aspect explicitly would be difficult but to enable an approximate assessment for future applications an option has been included which allows for a gradual linear decrease of the charging current parameter from k_t in the tip region to k_w on the walls over a specified distance. The default assumption which is used for the calculations in this report is that the transition from tip to walls is abrupt.

As indicated above there will be conditions for which the flux boundary conditions reduce to the constant concentration boundary condition. To test this prediction the numerical scheme was developed to include, optionally, constant concentration or flux boundary conditions. In the former case the concentration at the crack tip will be given by

$$C_t = C_o \exp \left\{ \frac{\bar{V}_H}{\sigma_{kk}} \right\} \quad (2.13b)$$

where C_o is the stress-free value. A similar expression is used for the walls.

Two forms of the stress distribution were considered in this analysis. In the case of the elastic solution represented by equation (1.1) it is necessary to consider incorporation of this singularity in stress as $r \rightarrow 0$. To overcome this problem the approach of Van Leuwen¹⁹ was used in which a blunt crack tip was assumed and the origin of the elastic stress distribution was shifted by the crack tip radius from the crack tip, thus giving a finite value at the tip itself (Figure 1b). Van Leewen actually assumed a shift in origin of half the crack tip radius but there are clear advantages in this analysis by setting the origin at one radius distance. This ensures that the stress gradient and flux at the boundaries are essentially parallel.

The second form of the stress distribution involved the assumption of a stress given by equation (1.2) in the region $0 < r < r_p$ and the use of equation (1.1) for values of $r > r_p$. Thus, the stress will be independent of r for $r < r_p$ but will vary with θ . It should be noted that $\nabla^2 \sigma_{kk} = 0$ for the pure elastic analysis equation (1.1) but is non-zero when plasticity is considered as in equation (1.2)

2.2 SCALING OF EQUATIONS

For ease of mathematical analysis it is convenient to express the conservation equations in dimensionless form. Defining $\tau = Dt/a^2$, $X = x/a$, $Y = y/a$, $u = C/C_N$, $v = N_r\theta_r/C_N$, $w = N_i\theta_i/C_N$, $\lambda = N_rk_1a^2/D$, $\mu = p_1a^2/D$, $\kappa = N_ik_1a^2/D$, $\rho = C_N/N_r$, $\nu = C_N/N_i$, $S = \sigma_{kk}/\sigma_y$, $\alpha_s = \bar{V}_H\sigma_y/R_gT$, equations (2.1) to (2.5) become (with $\partial N/\partial t = 0$):-

$$\frac{\partial u}{\partial \tau} = \nabla^2 u + \alpha_s \nabla(-u \nabla S) - \frac{\partial v}{\partial \tau} - \frac{\partial w}{\partial \tau} \quad (2.14)$$

$$\frac{\partial v}{\partial \tau} = \lambda u (1 - \rho v) - \mu v \quad (2.15)$$

$$\frac{\partial w}{\partial \tau} = \kappa u (1 - \nu w)$$

where C_N is an arbitrary value of the hydrogen concentration and a is half the crack tip opening displacement.) The scaled parameter S is defined as $S = k \cos(\theta/2)/R^{1/2}$, where $R = r/a$ and $k = 2(1+\nu_p)K_I/[3\sigma_y(2\pi a)^{1/2}]$. The radius of the plastic zone will be given by R_p . The new scaled co-ordinate system is shown in Figure 1b.

Initial conditions

$$u = v = w = 0 \quad \text{at} \quad \tau = 0 \quad . \quad (2.17)$$

Boundary conditions

$$u = u_b \quad \text{on} \quad R = R_b$$

$$u = u_b \quad \text{on} \quad X = -L \quad . \quad (2.19)$$

Crack wall condition

$$-\frac{\partial u_w}{\partial Y} + \alpha_s u_w \frac{\partial S}{\partial Y} = \beta_w \left[\exp(\alpha_s S) \right] \theta_w - \alpha_w u_w = \gamma_w (1 - \theta_w) - \eta_w \theta_w^2 \quad (2.21)$$

Crack tip condition

$$\frac{\partial u_t}{\partial n} + \alpha_s u_t \frac{\partial S}{\partial n} = \beta_t \left[\exp(\alpha_s S) \right] \theta_t - \alpha_t u_t = \gamma_t (1 - \theta_t) - \eta_t \theta_t^2$$

where $\beta_w = k_1 a / DC_N$, $\alpha_w = k_{-1} a / D$, $\gamma_w = k_w a / DC_N$, $\eta_w = k_w^* a / DC_N$, $\beta_t = k_2 a / DC_N$, $\alpha_t = k_{-2} a / D$, $\gamma_t = k_t a / DC_N$, $\eta_t = k_t^* a / DC_N$.

To allow for a gradual transition between γ_t and γ_w on the crack walls the following piecewise linear relationship was used:

$$\begin{aligned}
x < -D_1 & \quad \gamma = \gamma_w \\
-D_1 \leq x \leq 0 & \quad \gamma = \gamma_t - \frac{x}{D_1} (\gamma_w - \gamma_t)
\end{aligned}$$

These were included for completeness in the model but in this report only calculations with $D_1 \rightarrow 0$ are used so that there is essentially an abrupt change from γ_t to γ_w .

It is shown in Appendix 3 that when α_t and β_t are very large (see previous discussion in relation to k_2 and k_{-2}), equation (2.22) becomes

$$\frac{\partial u_t}{\partial n} - \alpha_s u_t \frac{\partial S}{\partial n} = \eta_t \frac{\alpha_t^2 u^2}{\beta_t^2 \exp(2\alpha_s S)} - \gamma_t$$

A similar expression is used for the wall condition. A detailed treatment of the stress gradient terms is given in Appendix 4. For constant concentration boundary conditions, $u = u_w$ on the crack walls and $u = u_t$ at the crack tip. To account for hydrostatic stress:

$$u_t = u_o \exp(\alpha_s S)$$

where u_o is the stress free value (with a similar expression for u_w).

3 NUMERICAL TREATMENT

The mathematical definition of the problem under consideration is given by the diffusion equation (2.14), the trapping equations (2.15) and (2.16), the boundary conditions (2.21) and (2.22) and conditions (2.18) and (2.19) defining u around the boundary at some distance from the crack region. For purposes of this section, it is assumed that the scaled stress function S is a known function of position and that α , λ , μ , κ , ρ and v are known constants.

Although equations (2.15) and (2.16) contain no spatial derivatives, they contain u which satisfies the partial differential equation (2.14), thus all three quantities u , v and w are functions of time and position. The problem is non-linear in character due to the presence of the non-linear term in condition (2.23) and the uv and uw terms in equations (2.15) and (2.16) respectively. In general, the geometry of the crack and the surrounding boundary will be irregular such that description of the region of interest in terms of a regular co-ordinate system is impossible. To summarise, the problem is unsteady, two-dimensional, non-linear and takes place over an irregular region; it thus represents a significant computing problem. The greater part of this section will describe the numerical treatment of the spatial aspects and the unsteady behaviour of the trapping functions as described by (2.15) and (2.16).

3.1 SPATIAL ASPECTS

Numerical treatment of irregular geometry is most commonly undertaken by finite element analysis; numerous commercial packages are available for use on both microcomputers and mainframe machines. The PAFEC system implemented on the NPL mainframe can readily treat unsteady heat transfer problems, but special features of the present problem could not be handled without considerable system development arranged through a sizable consultancy

agreement. These features include non-linear boundary conditions, unsteady source terms described by differential equations and the effects of the transport terms in (2.14) involving the gradient of the species concentration. For this reason it was decided to develop in-house software for the numerical solution of this problem. In order to overcome the difficulty associated with the irregular geometry it was decided to use the method of boundary fitted co-ordinates (BFC)^{29,30}. Essentially this technique performs a numerical transformation from the physical domain (such as that shown in Figure 1b) to a rectangular domain. The transformed governing equations are then solved using conventional finite difference methods. Unfortunately, the transformed equations are generally more complicated than those of the original set, but this is considered a small price to pay for the benefits of working in a rectangular domain. Details of the technique are given in references 29 and 30; here we present only the main features.

The physical plane (X,Y) is transformed to the (ξ,η) plane by the transformation $\xi = \xi(X,Y)$, $\eta = \eta(X,Y)$. The inverse transformation is given by $X = X(\xi,\eta)$, $Y = Y(\xi,\eta)$. Derivatives are transformed as

$$f_X = \frac{(Y_\eta f_\xi - Y_\xi f_\eta)}{J}$$

$$f_Y = \frac{(-X_\eta f_\xi + X_\xi f_\eta)}{J}$$

where J is the Jacobian of the transformation, $J = X_\xi Y_\eta - X_\eta Y_\xi$. The aim is to choose a transformation function such that boundaries are coincident with co-ordinate lines; we choose

$$\xi_{XX} + \xi_{YY} = 0$$

and

$$\eta_{XX} + \eta_{YY} = 0$$

with constant Dirichlet boundary conditions. In the present case, the physical (X,Y) plane of Figure 1b is transformed to the (ξ,η) plane of Figure 2. Here AB transforms to $A'B'$, BC to $B'C'$, CD to $C'D'$ and DA to $D'A'$. In order to perform computations in the rectangular transformed plane, it is necessary to interchange the dependent and independent variables of (3.3) and (3.4); these become

$$\alpha X_{\xi\xi} - 2\beta X_{\xi\eta} + \gamma X_{\eta\eta} = 0$$

$$\alpha Y_{\xi\xi} - 2\beta Y_{\xi\eta} + \gamma Y_{\eta\eta} = 0$$

where

$$\left. \begin{aligned} \alpha &= X_{\xi}^2 + Y_{\eta}^2 \\ \beta &= X_{\xi}X_{\eta} + Y_{\xi}Y_{\eta} \\ \gamma &= X_{\xi}^2 + Y_{\xi}^2 \end{aligned} \right\}$$

The boundary conditions of (3.3a) and (3.3b) are supplied by the boundary definition of the original problem; for example mesh points along AB of Figure 1b are defined by $Y = 0$ with X taking values between 1 and R_b . Similarly on boundary BC, X and Y are given by $X = R_b \cos \theta$, $Y = R_b \sin \theta$ with θ taking suitable values. Equations (3.3a) and (3.3b) can be readily solved using Successive Over Relaxation (SOR) to yield X and Y on a rectangular mesh in the (ξ, η) plane. The co-ordinate system thus generated has constant η -lines corresponding to AB and DC in the original problem and constant ξ -lines corresponding to AD and BC. A 20×20 mesh for preliminary calculations is shown in Figure 3. Here $R_b = 20$ and $L = 12$ and the points on $Y = 0$ are distributed according to a quadratic function so as to increase the mesh density in the region of the crack tip.

The governing partial differential equation must be expressed in terms of the new variables. Equation (2.14) is of the form

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial X^2} + \frac{\partial^2 u}{\partial Y^2} + D \frac{\partial u}{\partial X} + E \frac{\partial u}{\partial Y} + Fu + G$$

where D and E involve the gradients of the stress function and F and G involve the trapping functions v and w . It can be shown³⁰ that (3.4) transforms to

$$J^2 \frac{\partial u}{\partial \tau} = \alpha \frac{\partial^2 u}{\partial \xi^2} - 2\beta \frac{\partial^2 u}{\partial \xi \partial \eta} + \gamma \frac{\partial^2 u}{\partial \eta^2} + J(DY_{\eta} - EX_{\eta}) \frac{\partial u}{\partial \xi} + J(EX_{\xi} - DY_{\xi}) \frac{\partial u}{\partial \eta} + J^2 Fu + J^2 G \quad (3.5a)$$

where α , β and γ are given by (3.4) and J denotes the Jacobian. Clearly (3.5a) is considerably more complex than (3.5), but the main complication is the appearance of the cross derivative term. This has significant bearing on the choice of numerical algorithm. In the absence of this term, the most efficient technique is probably the Alternating Direction Implicit (ADI) method which involves consecutive solution of tridiagonal systems of linear equations. However, the presence of the cross derivative term destroys the tridiagonal property thus removing one of the main advantages of the method. This term could be treated as a source term, but overall convergence could be adversely affected if this term were comparatively large. It was decided finally to use a fully implicit time discretisation and SOR to solve the resulting equations. This choice is clearly not the most efficient of computer time but has the advantage of ease of coding and convenience in that iterations for the transformed non-linear condition (2.23) and the trapping functions can be incorporated readily.

3.2 TRAPPING EQUATIONS

The trapping equations (2.15) and (2.16) can be re-written as

$$\frac{\partial v}{\partial \tau} + v (\lambda \rho u + \mu) = \lambda u$$

$$\frac{\partial w}{\partial \tau} + w\kappa v u = \kappa u.$$

We let $dp/d\tau = \lambda\rho u + \mu$ and $dq/d\tau = \kappa v u$; then (3.6) is

$$\frac{\partial}{\partial \tau} (v e^P) = \lambda u e^P$$

and so

$$v = \lambda e^{-P(\tau)} \int_0^\tau e^{P(s)} u(s) ds$$

where we have assumed $v = 0$ when $\tau = 0$.

Similarly

$$w = \kappa e^{-Q(\tau)} \int_0^\tau e^{Q(s)} u(s) ds.$$

Over a small time interval $[\tau_j, \tau_{j+1}]$ we can write (3.8) as

$$v_{j+1} e^{P_{j+1}} - v_j e^{P_j} = \lambda \int_{\tau_j}^{\tau_{j+1}} e^{P(s)} u(s) ds.$$

If we assume that p and u vary linearly over this small interval, the integral on the right hand side can be performed analytically; after some algebra and re-arrangement we obtain

$$v_{j+1} e^{P_{j+1}} = v_j e^{P_j} + \frac{\lambda}{p'} \left(u_{j+1} e^{P_{j+1}} - u_j e^{P_j} \right) - \frac{\lambda u'}{(p')^2} (e^{P_{j+1}} - e^{P_j})$$

where

$$u' = \frac{u_{j+1} - u_j}{\Delta\tau}, \quad p' = \frac{P_{j+1} - P_j}{\Delta\tau} \quad \text{and} \quad \Delta\tau = \tau_{j+1} - \tau_j$$

In this way, (3.10) can be used to obtain values for v at the new time level in terms of values of the variables at the old time level. A similar expression can be obtained for w_{j+1} from (3.9). These expressions take full account of the exponential character of the solutions to (3.6) and (3.7) and are capable of producing more accurate solutions than simpler formulae if λ, κ etc are large.

The complete numerical scheme is implemented as follows:-

- Equations (3.3a) and (3.3b) are solved to give X and Y in terms of the new variables (ξ, η) .
- Assuming initial values for v and w , one SOR sweep of equation (3.5a) is performed to obtain an estimate to u at the new time level.

- c) Equation (3.10) and a similar equation for w are used to obtain estimates to v and w at the new time level.
- d) Steps (b) and (c) are repeated until u , v and w have converged sufficiently over this time interval.
- e) The time level is incremented and the whole process is repeated until the total required time range has been covered.

4 RESULTS AND DISCUSSION

In view of the complexity of the problem and the introduction of a comparatively novel numerical approach in relation to this type of problem, it is essential to proceed stepwise through the different stages of development and ensure confidence in prediction at each stage. Accordingly, we will describe first a simple diffusion problem with a constant wall boundary condition involving no stress or trapping. This will be used to verify the BFC technique by comparing results with those obtained using another numerical method. The effect of flux boundary conditions and the influence of hydrostatic stress will be considered subsequently. Trapping effects will be considered last.

In view of the preliminary nature of this work, the computations are intended to illustrate the effect of different assumptions (eg boundary conditions) and not to be an exhaustive evaluation of all the different variables and their magnitude.

4.1 VERIFICATION OF THE BOUNDARY FITTED CO-ORDINATE METHOD

In order to validate the computer program, it was decided to compare results for a test problem with those obtained using an independent method. The test problem involved the solution of Laplace's equation within the region shown in Figure 1b with $R_b = 20$ and $L = 16$. Boundary conditions for this case were as follows; $u = 1$ on AE (tip region), $\partial u / \partial Y = 0$ on AB (symmetry) and u equal to zero on the remainder of the boundary. A definitive numerical calculation was performed using a boundary integral equation (BIE) technique (for a description see, for example, reference (31) which is ideally suited to problems governed by Laplace's equation. The value of u at $X = 1.19$, $Y = 0$ obtained using this technique was 0.912; this was compared with results computed using boundary fitted co-ordinates. Table 1 shows results corresponding to various mesh densities. For all runs, mesh points were distributed quadratically on AB such that

$$X_i = 1 + (R-1) (i/m)^2 \quad i = 0, 1, \dots, m \quad (4.1)$$

The region AE around the crack tip was described by $n/5$ equispaced mesh points and ED by $4n/5$ points; meshes were uniformly spaced around the remainder of the boundary. The table of results indicates that the number of mesh points in the Y-direction (n) has a significant effect; this most likely reflects the requirement for a fine mesh near the crack tip to resolve local geometric effects and the presence of the discontinuity in u at position E. The use of a graduated mesh in this region would most likely be beneficial. The table shows that 3% accuracy can be obtained using 20×40 points. With 30×50 points the error reduces to about 2%. On the basis of these calculations, it was concluded that the BFC program is capable of more than adequate accuracy provided that a suitable meshing strategy and mesh density are adopted.

Comparison of results obtained from finite element (FE) analysis using PAFEC were also made with those from BFC and BIE for the same boundary conditions. The results are

shown in Figure 4 and indicate satisfactory agreement between the three procedures for this mesh density.

The construction of the mesh required modification when extending the calculations to incorporate flux boundary conditions and larger values of R_b . An example of the mesh distribution for $R_b = 200$ is illustrated in Figures 5(a) and (b). The features of this distribution include equi-spaced points around the tip; equi-spaced points on the walls and along the line $Y = 0$ for a specified distance (R_1) with a spacing which could be related variably to that at the tips. For distances greater than R_1 mesh lengths were increased according to a power law. The example shown in Figure 5(b) has eight equidistant points around the tip and eight equidistant points on $Y = 0$ out to about $X = 2.6$.

The choice of parameters depended on the severity of the problem and the required accuracy of the solution. For the majority of these calculations the use of eight equidistant points on the wall, around the tip and on $Y = 0$ with the rest distributed using a power law with exponent 2.15 was found to be near optimum for a balance between accuracy and economy. This gave results which were accurate to 25%, defined in relation to the convergent solution to the concentration at the crack tip (at which differences due to meshing are greatest) determined by progressively increasing the mesh density.

4.2 EFFECT OF BOUNDARY CONDITIONS ON HYDROGEN DISTRIBUTION

4.2.1 No stress

In order to clarify the effect of stress on crack tip concentrations, initial computations were made with zero hydrostatic stress but with the crack opening identical to that for the stressed system discussed in the next section. At this stage, trapping is not incorporated explicitly. Calculations were made for constant concentration and for flux boundary conditions at the crack tip using the parameters defined in Appendix 5 with $R_b = 200$. The results are shown in Figure 6 in terms of the variation of concentration in the X direction, along the line $Y = 0$, for varying values of the defined concentration at the outer boundary (u_b). By definition, the constant concentration boundary condition yields $u = 1.0$ at the crack tip. Identical results are obtained for flux boundary conditions but only if α and γ are both very large (see Appendix 3, equation (A2.8)). On the walls of the crack the value of γ_w was taken to be $0.1 \gamma_t$ and for the constant concentration condition $u_w = 0.3$. This value of u_w was chosen to be compatible with the solution for the flux boundary conditions at high values of γ and α .

The results shown for the flux boundary conditions in Figure 6 using values of γ_t more relevant to low alloy steels indicate that the predicted crack tip concentration is considerably different from that associated with constant concentration with the extent being dependent on the outer boundary condition. In calculating γ_t , the charging current density at the tip was taken to be about 4.8 Am^{-2} which is in excess of estimated values²⁷. Nevertheless, this value was chosen to be conservatively large to demonstrate unequivocally the importance of adopting flux boundary conditions. The choice of the position of the outer boundary is important because the reduced concentration gradient at "steady-state" associated with an increased value of R_b , ($u_b = 0$) will be expected to increase the crack tip concentration. In practice the effect of increasing R_b on crack tip concentration is relatively modest. For R_b increasing as $R_b = 20, 200, 400, 600$ and 1000 , the value of u_t increases as $0.23, 0.27, 0.30$ and 0.32 respectively. This is a result of the boundary conditions on the crack walls which create a concentration gradient from the tip to the walls. The choice of $R_b = 200$ is not unreasonable for these preliminary calculations.

An interesting feature of the results for constant concentration boundary condition with $u_b = 1.0$ is the initial decrease of concentration from the value of 1.0 at the tip before rising

to 1.0 at the outer boundary. This serves to emphasise further the effect on concentration of the gradient of hydrogen towards the crack walls, which is not surprising since the crack wall represents the closest boundary to the tip.

The value of $u_b = 10$ is based on the assumption²⁷ of bulk charging of low alloy steel with hydrogen under cathodic polarisation conditions at potentials of about -1100 mV (SCE). The position of the boundary for this case cannot be specified exactly in relation to the real situation but is chosen sufficiently remote from the tip that the value will not be strongly influenced by the conditions at the tip. It will be noted that for conditions of bulk charging there is a net flux of hydrogen out of the crack tip, which will have the effect of increasing θ_t .

4.2.2 Truncated stress

The effect of hydrostatic stress on the concentration profiles is illustrated in Figures 7 and 8. A stress intensity factor of $10 \text{ MPa m}^{1/2}$ was selected. The maximum increased concentration expected from equation (1.2) and (2.13b) is 2.86, assuming that the truncation is made at the edge of the plastic zone. This increased concentration is obtained (by definition) with the fixed concentration boundary condition (ie time-invariant). However, for the flux boundary condition with $u_b = 0$ the value of u_t increases only from 0.23 to 0.33 ($R_b = 200$) due to stress because the supply kinetics are limiting the achievable concentration. The value of u_t does increase with increasing R_b with values of 0.33, 0.41, 0.45 and 0.49 obtained for $R_b = 200, 400, 600$ and 1000 respectively. The crack tip concentration converges to a near constant value which it is still significantly less than would be calculated based on fixed concentrations at the crack tip. This further emphasises the importance of the crack walls as a sink for hydrogen atoms. The results also indicate that future calculations should be based on $R_b \geq 400$. When $u_b = 10$ the effect of stress on crack tip concentration is much greater (comparing Figures 6 and 7) though not quite attaining the maximum relative increase possible. Indeed equation (2.24), would predict an equilibrium lead value of u_t of order 28.6 if the system were initially pre-charged to a value of $u = 10$. A practical case most representative of this situation is perhaps a pre-charged sample with a cadmium coating which is relatively impermeable to hydrogen. As soon as crack tip straining was sufficient to cause rupture of this coating, the assumption of zero flux would no longer be valid and indeed a very large concentration gradient and local flux would be generated diminishing the crack tip concentration.

For completeness, the variation of hydrogen concentration around the crack tip is shown in Figure 8. The distribution in this direction is influenced by the variation in hydrostatic stress as well as by the changing boundary condition on moving from the tip to the crack walls.

The results above demonstrate that assessment of the effect of hydrostatic stress on crack tip concentrations cannot be deduced from a simple equilibrium relationship since this is based on the assumption of zero flux. More account must be taken of the flux of species in the crack-tip region. However, these calculations are based on parameters for low alloy steels. With alloys of much lower lattice diffusivity such as the face-centred cubic alloys much closer agreement is obtained. For example, for nickel alloys³² with a lattice diffusion coefficient of $D = 6.3 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ the crack tip concentration at steady state achieves the value of 2.86 ($u_b = 0$) which is exactly the predicted equilibrium value. However, when the sample is precharged ($u = 10$) the crack tip concentration obtained is also 2.86 which is considerably less than the equilibrium value of 28.6. The value of 2.86 is independent of the precharged value and depends only on the balance of kinetics and diffusion at the tip represented in the flux boundary conditions.

4.2.3 Near-elastic stress

The approach to near-elastic stresses is made by progressively decreasing the value of R_p with the largest value of hydrostatic stresses at the tip being obtained for $R_p = 0$. The stress is still finite because the origin of the elastic stress distribution is shifted from the crack tip to the extent of one crack tip radius. The normalised stresses for different values of R_p are shown in Figure 9. The predicted maximum value of u_t will vary according to the value of S at the tip (equation 2.24). For $R_p = 0$ a value of $u_t = 5.5 \times 10^3$ is predicted while for $R_p = 1.5$ and 6.7 values of 1.1×10^3 and 2.8×10^1 are expected based on the assumption of equilibrium (equation 2.24).

In practice, the results shown in Figure 9 suggest a complex dependence on the value of R_p . The maximum concentration is obtained at $R_p = 0$ but the value of $u_t = 4.9$ is three orders of magnitude smaller than the equilibrium value again reflecting the limitations imposed by the flux boundary conditions.

When the stress is truncated the concentration at the tip is observed to be lowest for the smallest value of R_p which was unexpected. The explanation is most likely associated with the zero stress gradient at the tip so that from equation (2.10) the crack tip flux depends only on the concentration gradient. For the case of $R_p = 0$ the stress gradient is non-zero and through equation (2.10) the associated flux term will be opposite in sign to that associated with diffusion driven by the concentration gradient. Hence, the flux will be less for the elastic case.

With increasing value of R_p the stress gradient diminishes and through equation (2.1) this tends to reduce the rate of depletion of hydrogen with the consequence that the crack tip value increases. Calculations using the lattice diffusion coefficient for nickel with $R_p = 0$ yielded a value of $u_t = 4.3 \times 10^3$ which is close to the equilibrium value of 5.5×10^3 emphasizing the significance of the diffusion flux in determining crack tip concentration and also the need to incorporate flux boundary conditions when evaluating hydrogen atom distribution at crack tips in low alloy steels. The detailed nature of the stress distribution at the crack tip, in particular stress gradient, is also important.

4.3 TIME-DEPENDENT TRANSPORT

The preceding analysis has been concerned with steady-state conditions albeit with an outer boundary which is not too far removed from the crack tip. The time-evolution of the concentration of hydrogen will depend on assumptions made concerning trapping. For this stage of analysis the trap density is assumed to be uniform in the material. A detailed evaluation of trapping behaviour would be premature in the context of this report which is mainly concerned with setting out the general approach with appropriate examples. Nevertheless, it is pertinent to demonstrate the influence of trapping on transport.

Figure 10 shows the variation of concentration along the x-axis ($y=0$) at varying times for both lattice diffusion and diffusion with reversible trapping at low trap occupancy. The steady-state concentration is shown for comparison. The key parameter is the ratio λ/μ and a value of 10^3 would be appropriate for a low alloy quenched and tempered steel.

The results of Figure 10 serve to demonstrate the delay associated with trapping. In addition, nearly equivalent profiles are obtained at times which are displaced in the case of trapping by approximately the factor of $\lambda/\mu=10^3$ relative to the pure lattice diffusion case. Since trap occupancy was assumed negligible for this particular example this agreement is anticipated because the use of an effective diffusion coefficient ($D_{\text{eff}} = D/(1 + \lambda/\mu)$) is then applicable. In other words, the solution based on diffusion only, but with a modified definition of D and hence of τ , could be utilised for this specific case.

It should be noted that in real time these values for $\tau = 8.9 \times 10^6$ are very short indeed and of the order of only 15 secs. The plastic zone size is only 7 μm and hence near-steady conditions in this region might be expected rapidly even with an outer boundary positioned at much greater distances than represented in Figure 10.

5 CONCLUSIONS

The boundary fitted co-ordinate method can be applied successfully to analysis of transport in complex geometries. Results were validated by comparison with boundary integral and finite element methods.

The use of flux boundary conditions at the crack tip and walls is advisable for reliable prediction of the effects of precharging and of crack-tip stress on crack-tip hydrogen concentration profiles in low alloy steels. For this reason published models based on the assumption of constant concentration or zero flux boundary conditions may be unsatisfactory for these steels.

The use of constant concentration boundary conditions based on the assumption of equilibrium between adsorbed and absorbed states and a constant value of the surface coverage of hydrogen atoms can be more reasonable for alloys of low lattice diffusion coefficient for hydrogen such as the face-centred cubic alloys. However, this does not apply to precharged conditions for which flux boundary conditions must be adopted.

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APPENDIX 1

NOMENCLATURE

a	half the crack tip opening displacement ($0.3 (1-\nu_p)^2/E\sigma_y$)
C	lattice hydrogen concentration
C_b	lattice hydrogen concentration on outer boundary
C_{H^+}	hydrogen ion concentration
C_N	arbitrary value of the hydrogen concentration used for normalisation
C_o	stress-free value of the crack tip hydrogen concentration
C_r, C_i	hydrogen concentration of reversible and irreversible trap sites respectively
C_w, C_t	subsurface lattice hydrogen concentration on the crack walls and crack tip respectively
D	lattice diffusion coefficient
D_1	distance over which transition from crack tip current to crack wall current occurs
ΔE	binding energy of the reversible trap site
E	electrode potential
F	Faraday constant
	hydrogen flux through the crack walls and crack tip
K_I	mode I stress intensity factor
k_1, k_2	absorption rate constants for the crack walls and crack tip
k_{-1}, k_{-2}	desorption rate constants for the crack walls and crack tip
k_r, k_i	capture rate constant for reversible and irreversible trap sites respectively
k_t, k_w	reaction rate parameter defining the electrochemical generation of hydrogen atoms on the crack tip and crack walls respectively (see equation 2.11)
k_t^*, k_w^*	rate constant for recombination of hydrogen atoms on the crack walls and crack tip
N_L	number of lattice site per unit volume
	density of reversible and irreversible trap sites respectively
p_r	release rate for reversible trap sites
R_g	gas constant
r_b	distance to outer boundary from crack tip
r_p	size of the plastic zone ($(K_I/\sigma_y)^2/3\pi$)
R_b	normalised distance to outer boundary from crack tip
R_p	r_p/a
R	r/a

R_1	specified distance along $y = 0$ for which meshing is equi-spaced
S	normalised hydrostatic stress (σ_{kk}/σ_y)
T	absolute temperature
t	time
u	normalised lattice hydrogen concentration (C/C_N)
u_b	normalised lattice hydrogen concentration on outer boundary (C_b/C_N)
u_o	normalised stress-free value of the crack tip hydrogen concentration (C_o/C_N)
u_w, u_t	normalised subsurface lattice hydrogen concentration on the crack walls and crack tip respectively
v	normalised hydrogen concentration of reversible trap sites ($N_r\theta_r/C_N$)
$\bar{V}_H$	partial molar volume of hydrogen
w	normalised hydrogen concentration of irreversible trap sites ($N_i\theta_i/C_N$)
α_s	$\bar{V}_H\sigma_y/R_gT$
α_w, α_t	normalised absorption rate constants for the crack walls and crack tip ($k_1/D, k_2a/D$)
β	transfer coefficient
	normalised desorption rate constants for the crack walls and crack tip ($k_1a/DC_N, k_2a/DC_N$)
	normalised reaction rate parameter on the crack walls and crack tip ($k_wa/DC_N, k_ta/DC_N$)
Δ	spacing of mesh around crack tip normalised with respect to a normalised rate constant for recombination of hydrogen atoms on the crack walls and crack tip ($k_w^*a/DC_N, k_t^*a/DC_N$)
θ_r, θ_i	fractional occupancy of reversible and irreversible trap sites
θ_w, θ_t	surface coverages of hydrogen atoms on the crack walls and crack tip
κ	normalised capture rate constant of hydrogen per irreversible trap site ($N_i k_i a^2/D$)
λ	normalised capture rate constant of hydrogen per reversible trap site ($N_r k_r a^2/D$)
μ	normalised release rate for reversible trap sites ($p_r a^2/D$)
ν	C_N/N_i
ν_p	Poisson's ratio
ρ_c	crack tip radius
ρ	C_N/N_r
	hydrostatic stress
σ_y	yield stress
τ	normalised time (Dt/a^2)

ψ ratio of mesh spacing along $y = 0$ (equi-spaced meshes) to spacing around tip

APPENDIX 2

EVALUATION OF THE RATE CONSTANTS FOR THE FLUX
BOUNDARY CONDITIONS

Hydrogen entry into the metal may be represented in terms of the flux

$$J = -D \nabla C_o = k_{abs} \theta - k_{des} C_o \quad (A1.1)$$

where θ is the surface coverage of hydrogen atoms and C_o is the sub-surface concentration of atoms. A methodology for determining the ratio of absorption and desorption rate constants (k_{abs} and k_{des}) has been outlined by Iyer and Pickering²⁸.

Let the charging current density be represented by

$$i = k[H^+] (1-\theta) \exp \left[- \frac{\beta F E}{R_g T} \right] \quad (A1.2)$$

where β is the transfer coefficient and E is the electrode potential.

The recombination current density, assuming chemical recombination, may be written

$$i_r = F k_r \theta^2 \quad (A1.3)$$

Thus

$$= i_c - i_r \quad (A1.4)$$

At steady state the permeation current density, i_p^{ss} , is given by

$$i_p^{ss} = \frac{F D C_o^{ss}}{L} \quad (A1.5)$$

where D is the lattice diffusion coefficient of hydrogen atoms and L is the thickness of membrane used experimentally. Also, at steady-state (assuming the flux is relatively small compared to i_c and i_r)

$$\frac{C_o}{\theta} = K = \frac{k_{abs}}{k_{des}} \quad (A1.6)$$

Combining (A2), (A5) and (A6) with the assumption of constant $[H^+]$ for the period of interest, it follows that

$$i_c = k_c \exp \left\{ -\frac{\beta FE}{R_g T} \right\} \left[1 - \frac{i_p^{ss} L}{KDF} \right]. \quad (A1.7)$$

Hence, a plot of $i_c \exp \{\beta FE/RT\}$ against i_p^{ss} should yield a slope of $-k_c L/KDF$ and intercept of k_c from which K can be derived.

Now using equation (A3) and (A6) it follows from equation (25) that

$$i_p^{ss} = \frac{FD}{L} \frac{K}{(Fk_r)^{1/2}} i_r^{1/2}. \quad (A1.8)$$

Thus, a plot of i_p^{ss} against $i_r^{1/2}$ should yield a value for k_r .

In this way, the key parameters can be determined by controlled experiments although the individual values of k_{abs} and k_{des} are less accessible. However, a useful approximation for modelling purposes is to assume that they are sufficiently large to ensure equilibrium at the interface for most of the timescale of relevance.

APPENDIX 3

REARRANGEMENT OF FLUX BOUNDARY CONDITIONS

For convenience the subscripts t and w are dropped in this appendix and $\beta \exp(\alpha_s S)$ is rewritten as β' . Using equation (2.22), the surface coverage can be expressed as

$$\theta = \frac{-(\beta' + \gamma) + [(\beta' + \gamma)^2 + 4\eta (\gamma + \alpha u)]^{1/2}}{2\eta} \quad (\text{A2.1})$$

$$\frac{2(\gamma + \alpha u)}{[\beta' + \gamma + [(\beta' + \gamma)^2 + 4\eta (\gamma + \alpha u)]^{1/2}]}$$

$$\therefore J = \alpha u - \frac{2\beta' (\gamma + \alpha u)}{[(\beta' + \gamma)^2 + 4\eta (\gamma + \alpha u)]^{1/2} + \beta' + \gamma} \quad (\text{A2.2})$$

For the reasons discussed previously k_2 and k_{-2} are assumed to be very large and thus $\beta \gg \gamma$. This enables (A2.2) to be approximated by

$$J = \alpha u - \frac{2\beta' (\gamma + \alpha u)}{[\beta'^2 + 4\eta (\gamma + \alpha u)]^{1/2} + \beta'} = \alpha u - \frac{2(\gamma + \alpha u)}{\left[1 + 4\eta \frac{(\gamma + \alpha u)}{\beta'^2}\right]^{1/2} + 1} \quad (\text{A2.3})$$

Now for parameters of practical relevance $4\eta(\gamma + \alpha u)/\beta^2$ will be small, so the binomial approximation $(1+x)^n \approx 1+nx$ can be used: thus,

$$J \approx \alpha u - \frac{\gamma + \alpha u}{1 + \frac{\eta(\gamma + \alpha u)}{\beta'^2}} \quad (\text{A2.4})$$

Again, $\frac{\eta}{\gamma} (\gamma + \alpha u)$ is small, so

$$J \approx \alpha u - (\gamma + \alpha u) \left(1 - \frac{\eta}{\beta'^2} (\gamma + \alpha u)\right) \quad (\text{A2.5})$$

which reduces finally to

$$J = \frac{\eta}{\beta'^2} (\gamma + \alpha u)^2 - \gamma. \quad (\text{A2.6})$$

Rewriting β' as $\beta \exp(\alpha_s S)$ again and assuming α is very large:

$$J = \frac{\eta \alpha^2 u^2}{\beta^2 \exp(2\alpha_s S)} - \gamma. \quad (\text{A2.7})$$

With α and γ large, equation (A2.7) yields

$$u \sim \frac{\beta}{\alpha} \left(\frac{\gamma}{\eta} \right)^{1/2} \exp(\alpha_s S) \quad (\text{A2.8})$$

APPENDIX 4

DERIVATION OF STRESS TERMS IN EQUATION (2.14)

In the notation of Section 2.2, the scaled stress terms in equation (2.14) involve $\partial S/\partial X$, $\partial S/\partial Y$ and $\partial^2 S/\partial X^2 + \partial^2 S/\partial Y^2$. We assume that S varies in position according to

$$\frac{k}{\sqrt{\rho}} \cos(\psi/2), \quad \rho > \rho_o \quad (\text{A3.1a})$$

and

$$\frac{k}{\sqrt{\rho_o}} \cos(\psi/2), \quad \rho < \rho_o \quad (\text{A3.1b})$$

where (ρ, ψ) are radial co-ordinates with origin at $(d, 0)$ as shown in Figure A.1. The distance d (OO' in the Figure) is chosen to be less than unity so as to ensure that (A3.1a) has no singularity in the region of interest. From the diagram, we can see that

$$\rho^2 = (X-d)^2 + Y^2 \quad (\text{A3.2})$$

$$\text{and} \quad Y = r \sin \theta = \rho \sin \psi. \quad (\text{A3.3})$$

We consider first the case where $\rho > \rho_o$. Using (A3.2) and (A3.3) we can show that

$$\cos^2\left(\frac{\psi}{2}\right) = \frac{\rho + X - d}{2\rho}$$

and so from (A3.1a) we have

$$S^2 = \frac{k^2}{2\rho^2} (\rho + X - d). \quad (\text{A3.4})$$

Differentiation of (A3.4) with respect to x gives

$$2S \frac{\partial S}{\partial X} = \frac{k^2}{2\rho^2} \frac{\partial \rho}{\partial X} + 1 - \frac{k^2}{\rho^3} \frac{\partial \rho}{\partial X} (\rho + X - d)$$

Substituting in this equation for $\partial \rho / \partial X$ obtained from (A3.2), we have after some simplification

$$\frac{\partial S}{\partial X} = \frac{k^2}{4S\rho^4} (X - d + \rho) (\rho - 2X + 2d) . \quad (\text{A3.5})$$

Similarly, differentiation of (A3.4) with respect to y yields

$$\frac{\partial S}{\partial Y} = \frac{k^2}{4S\rho^4} Y (2d - \rho - 2X) . \quad (\text{A3.6})$$

For the case where $\rho < \rho_o$, we have instead of (A3.4)

$$S^2 = \frac{k^2}{2\rho\rho_o} (\rho + X - d) \quad (\text{A3.7})$$

Proceeding as before, we find

$$\frac{\partial S}{\partial X} = \frac{k^2 Y^2}{4\rho_o S \rho^3} \quad (\text{A3.8})$$

and

$$\frac{\partial S}{\partial Y} = \frac{-k^2 (X - d) Y}{4\rho_o S \rho^3} \quad (\text{A3.9})$$

Thus equations (A3.5), (A3.6), (A3.8) and (A3.9) together with (A3.2) enable the calculation of the scaled stress gradients as functions of X and Y .

We note finally that (A3.1a) is a solution of Laplace's equation; as this operator is invariant under any change of variable, it follows that for $\rho > \rho_o$

$$\frac{\partial^2 S}{\partial X^2} + \frac{\partial^2 S}{\partial Y^2} = 0$$

For $\rho < \rho_o$ we can show from (A3.1b) that

$$\nabla^2 S = \frac{1}{\rho^2} \frac{\partial^2 S}{\partial \psi^2} = \frac{-S}{4\rho^2} \quad (\text{A3.10})$$

This indicates that the non zero value of $\nabla^2 S$ constitutes a further source term in equation (2.14) for the region $\rho < \rho_o$.

APPENDIX 5

SPECIFIC PARAMETERS USED IN THE ANALYSIS

FLUX BOUNDARY CONDITION

The constants used for determining specific parameters for the flux boundary conditions are set out below.

Absorption and desorption constants at crack wall and crack tip:

Crack wall;

$$\begin{aligned} k_1 &= 1.0 \times 10^{11} \text{ mol (m}^2\text{s)}^{-1}, & k_{-1} &= 8.8 \times 10^9 \text{ ms}^{-1} \\ &5.0 \times 10^{-6} \text{ mol (m}^2\text{s)}^{-1}, & k_w^* &= 2.2 \times 10^1 \text{ mol (m}^2\text{s)}^{-1} \end{aligned}$$

Crack tip;

$$\begin{aligned} k_2 &= 1.0 \times 10^{11} \text{ mol (m}^2\text{s)}^{-1}, & k_{-2} &= 8.8 \times 10^9 \text{ ms}^{-1} \\ &5.0 \times 10^{-5} \text{ mol (m}^2\text{s)}^{-1}, & k_t^* &= 2.2 \times 10^1 \text{ mol (m}^2\text{s)}^{-1} \end{aligned}$$

This value of k_t would represent a time-averaged charging current density of about 4.8 A m^{-2} at the crack tip. In the normalisation of these parameters the value of C_N was selected such that $u_t = 1$ for conditions of zero stress, viz:

$$C_N = 1.71 \times 10^{-2} \text{ mol m}^{-3}$$

The crack tip blunting radius, a , was set at $1.1 \times 10^{-7} \text{ m}$ based on a σ_y of 1200 MPa and $K = 10 \text{ MPa m}^{1/2}$ and the lattice diffusion coefficient for pure iron, $D = 7.2 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, at $T = 293 \text{ K}$ was used.

Using these values, the normalised parameters for the flux boundary conditions on the crack tip and crack wall are as follows:

On the crack wall;

$$\alpha_w = 1.34 \times 10^{11} \quad \beta_w = 8.93 \times 10^{13} \quad \gamma_w = 4.43 \times 10^{-3}, \quad \eta_w = 1.96 \times 10^4$$

On the crack tip;

$$\alpha_t = 1.34 \times 10^{11}, \quad \beta_t = 8.93 \times 10^{11}, \quad \gamma_t = 4.43 \times 10^{-2}, \quad \eta_t = 1.96 \times 10^4$$

HYDROSTATIC STRESS

The constants used for determining hydrostatic stress were as follows:

$$\sigma_y = 1.2 \times 10^3 \text{ MPa}, \quad \nu_p = 0.3, \quad \bar{V}_H = 2.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

Using these values with $a = 1.1 \times 10^{-7} \text{ m}$, the normalised parameter $\alpha_s = 0.99$.

TRAPPING

The values of λ and μ used in the trapping analysis were respectively 1.94×10^{-4} and 1.94×10^{-7} . In most circumstances it is the ratio of these parameters which is critical. The individual values were based on $N_r = 1.7 \times 10^{17} \text{ mol m}^{-3}$, $k_r = 6.9 (\text{mol m}^{-3})^{-1} \text{ s}^{-1}$ and $p_r = 1.2 \times 10^{-1} \text{ s}^{-1}$.

**TABLE 1. COMPARISON OF RESULTS FOR THE SIMPLE DIFFUSION
PROBLEM WITH THE BIE VALUE OF 0.912. (SECTION 4.1)**

RESULTS AT $X = 1.19, Y = 0$

$m \quad n$	10	20	30	40	50
10	0.615	0.835	0.869		
20		0.840	0.876	0.888	
30		0.839	0.877	0.889	0.895