Transient Hydrogen Diffusion Analyses of a Surface Crack in a Three-Dimensional Body

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Abstract
In hydrogen diffusion in metals, we have to consider not only the hydrogen flux driven by hydrogen concentration but also the hydrogen flux driven by hydrostatic stress. Such hydrogen diffusion is a multi-physics problem coupled hydrogen diffusion with a stress field. We developed a three-dimensional computer program for a transient hydrogen diffusion analysis by combining an in-house three-dimensional finite element program for a hydrogen diffusion analysis with a general-purpose finite element computer program for a stress analysis. Using this computer program, we performed transient diffusion analyses of a surface crack in a finite plate under tensile load or bending moment, and clarified the hydrogen concentration around the periphery of a surface crack. We also made a discussion on the effect of hydrogen on the crack growth behavior under cyclic loading. As a result, it is concluded that hydrogen does not have a harmful effect on the leak-before-break.

1. Introduction
Related with environmental problems, attention is paid to hydrogen as a new energy source. Fuel cells will be utilized not only in domestic use but also in automobiles. When they are utilized in automobiles, we have to arrange hydrogen infrastructure such as hydrogen stations. We need to transport and reserve high-pressure hydrogen to maintain hydrogen infrastructure. Reservoirs and piping in hydrogen systems should be designed to endure the internal pressure of 70MPa. Under such high pressure, hydrogen embrittlement, reduction of ductility due to hydrogen, is one of the critical issues for structural integrity of high-pressure components such as reservoirs and piping in hydrogen systems [1].

Various kinds of mechanism for hydrogen embrittlement have been proposed so far. Among them, HEDE (Hydrogen Enhanced Decohesion) [2, 3] and HELP (Hydrogen Enhanced Localized Plasticity) [4] are typical ones. Although it is controversial which mechanism is adequate to explain hydrogen embrittlement, it can be accepted that the hydrogen concentration near a crack tip plays an important role in hydrogen embrittlement. Experimental data [1] show that the hydrogen absorbed in steel has the effect on the fatigue crack growth behavior and reduces the fatigue life. In such a case, the hydrogen concentration near a crack tip would affect the fatigue crack growth rate.

A lot of hydrogen diffusion analyses have been performed to obtain the hydrogen concentration near a crack tip. Among them, Yokobori [5] et al. solved a hydrogen diffusion equation taking account of the effect of stress gradient. In their analysis, they used an analytical form of an elastic-plastic stress field. On the other hand, Sofronis and McMeeking [6] performed a hydrogen diffusion analysis by coupling a finite element program for a hydrogen diffusion analysis with a finite element program for a stress analysis. Korm et al. [7] added a term representing the effect of plastic strain, which was not taken into account in the model used by Sofronis and McMeeking [6]. After that Sofronis et al. [8] proposed a model for hydrogen-induced softening effect [9] that represents the decrease in the initial yield stress due to hydrogen absorption, and performed the analysis of hydrogen induced localization of plastic flow for a plate under uniform tension. In this analysis, they obtained only the steady state value of hydrogen concentration. Sofronis et al. [10, 11] then performed a transient analysis of hydrogen diffusion, taking account of the elastoplastic stress field around a crack tip, the effect of plastic strain and the hydrogen-induced softening effect.

From the viewpoint of structural integrity of components in hydrogen systems, fatigue failure under hydrogen embrittlement is most important. In such a case, we need the hydrogen concentration near a crack tip under cyclic loading. Yokobori et al. [12] and Kotake et al. [13] performed such analyses.

All the studies mentioned above deal with two-dimensional problems. A surface or embedded crack in a three-dimensional body is important from the practical viewpoint. In the present paper, we develop a three-dimensional computer program for a transient hydrogen diffusion analysis by combining an in-house three-dimensional finite element program for a hydrogen diffusion analysis with a general-purpose finite element computer program for a stress analysis. Using the computer program developed in the present study, we perform transient diffusion analyses of a surface crack in a finite plate under tensile load or bending moment, and clarify the hydrogen concentration around the periphery of a surface crack. We also make a discussion on the effect of hydrogen on the crack growth behavior under cyclic loading and clarify the effect of hydrogen on the leak-before-break of high-pressure components.

2. Finite element formulation for hydrogen diffusion equation
The hydrogen diffusion equation used in the present study is based on Sofronis et al's study [10] and Krom et al's study [7]. The details of finite element formulation for a hydrogen diffusion equation are given in references [7] and [13]. Here we will show it briefly.

Hydrogen in metals can be classified into two kinds according as the sites occupied by hydrogen atoms, that is, the hydrogen atoms at the normal interstitial lattice sites and those at the trap sites such as dislocations, voids, vacancies and so on. The hydrogen concentration at the lattice sites and that at the trap sites are respectively denoted by C_L and C_T. C_T is related with the equivalent plastic strain

ε_p in accordance with Kumnic et al's experimental results [14]. When we assume an equilibrium relation between the population of the hydrogen atoms at the lattice sites and that at the trap sites based on Oriani's theory [15], the hydrogen concentration at the trap sites C_T is related with the hydrogen concentration at the lattice sites C_L. Hydrogen flux **J** is driven not only by the gradient of the hydrogen concentration at the lattice sites C_L but also by the gradient of the hydrostatic stress σ_h, and **J** is given by

$$\mathbf{J} = -D_L \nabla C_L + \frac{D_L C_L V_H}{RT} \nabla \sigma_h \tag{1}$$

where D_L is the diffusion coefficient of hydrogen at the lattice sites, V_H the partial molar volume of hydrogen, R the gas constant i.e. $8.3144\,\mathrm{J/(mol \cdot K)}$, and T is the absolute temperature. Using the relations mentioned above, we can derive a hydrogen diffusion equation, as follows [7]:

$$D^* \frac{\partial C_L}{\partial t} - \nabla \cdot \left(D_L \nabla C_L \right) + \nabla \cdot \left(\frac{D_L C_L V_H}{RT} \nabla \sigma_h \right) + \theta_T \frac{\partial N_T}{\partial \varepsilon_p} \frac{\partial \varepsilon_p}{\partial t} = 0 \tag{2}$$

where θ_T is occupancy of the trap site, N_T the trap site density and D^* is the nondimensional diffusion coefficient defined by C_L, C_T and θ_T, as follows:

$$D^* = \frac{C_L + C_T(1 - \theta_T)}{C_L} \tag{3}$$

According to the standard finite element formulation using the Galerkin method, we can obtain the finite element hydrogen diffusion equation with an unknown vector for the hydrogen concentration at the lattice sites $\{C_L\}$, as follows:

$$[M] \frac{\partial \{C_L\}}{\partial t} + \left([K_1] + [K_2] \right) \{C_L\} = \{F_1\} + \{F_2\} \tag{4}$$

where the respective matrices and vectors are given by

$$[M] = \int_V [N]^T D^* [N] \mathrm{d}V \tag{5}$$

$$[K_1] = \int_V [B]^T D_L [B] \mathrm{d}V \tag{6}$$

$$[K_2] = -\int_V [B]^T \frac{D_L V_H}{RT} [B] \{\sigma_h\} [N] \mathrm{d}V \tag{7}$$

$$\{F_1\} = -\int_S [N]^T \{\phi\} \mathrm{d}S \tag{8}$$

$$\{F_2\} = -\int_V [N]^T \{\theta_T\} \frac{\partial N_T}{\partial \varepsilon_p} \frac{\partial \varepsilon_p}{\partial t} \mathrm{d}V . \tag{9}$$

In the above equations, $[N]$ is the shape function of a finite element, $[B]$ the gradient of $[N]$, that is, $[B] = \nabla [N]$, $\{\phi\}$ the hydrogen flux vector on the surface with an outward normal unit vector **n**, that is, $\phi = \mathbf{J} \cdot \mathbf{n}$, $\{\sigma_h\}$ the nodal hydrostatic stress vector, and $\{\theta_T\}$ denotes the nodal vector for occupancy of the trap site.

We can perform a transient hydrogen diffusion analysis by solving Eq.(4). The backward difference method was emplyed to discretize the time-derivative of $\{C_L\}$ in Eq.(4). As shown in Eqs.(7) and (9), we need stress and strain fields to solve the hydrogen diffusion equation. In the present study, they are obtained

from a commercial finite element software package MSC MARC. In the analysis, we considered the effect of hydrogen on the yield stress σ_Y, as follows:

$$\sigma_Y\left(\varepsilon_p, c\right) = \left(\xi \cdot c + 1\right)\sigma_0 \cdot \left(1 + \frac{\varepsilon_p}{\varepsilon_0}\right)^n \tag{10}$$

where σ_0 is the initial yield stress, c the total hydrogen concentration, ε_0 the initial yield strain, and n is the work-hardening parameter. ξ denotes a coupling parameter representing the effect of hydrogen on the yield stress. Hydrogen-induced softening occurs in case of $\xi < 0$, and hydrogen-induced hardening occurs in case of $\xi > 0$. We also considered large deformation around a crack tip. So we selected the option for the elastoplastic and large deformation analysis in MSC MARC code.

3. Analysis model

In the present analyses, we used the material properties for pure iron (α-Fe) at the temperature of 300K. Table 1 summarizes these material properties. α-Fe has the bcc structure at this temperature. The diffusion coefficients for bcc metals are 10^3 or 10^4 times larger than those of fcc and hcp metals [16]. Altough we can perform the hydrogen diffusion analysis considering the hydrogen-induced material sfotening effect by taking the negative value of ξ, the analysis for $\xi = 0$ provides the conservative results, that is, larger hydrostatic stress σ_h and hydrogen concentration C_L around a crack tip, compared with the analysis results taking account of the hydrogen-induced material sfotening effect [13, 17]. So the coupling parameter ξ was equal to zero for all analyses in the present study.

Hydrogen diffusion analyses were performed for a finite plate with a semi-elliptical surface crack. Fig. 1 shows a quarter of the plate that includes a semi-elliptical surface crack with a long radius of α and a short radius of β, the dimensions of which are given in Table 2. As shown in Fig. 2, two kinds of load, a uniform tensile load σ and a uniform bending moment M, were considered in the present analyses. A uniform tensile load σ of 200MPa was applied in the former case, while a bending moment M corresponding to the bending stress σ_b

Table 1 Material properties for pure iron (α-Fe) at the temperature of 300K

Material density ρ [kgm^{-3}]	7.87×10^3
Young's modulus E [GPa]	207
Poisson's ratio ν	0.3
Initial yield stress σ_0 [MPa]	250
Work hardening exponent n	0.2
Lattice sites per unit volume N_L [m^{-3}]	5.1×10^{29}
Lattice diffusivity D_L [m^{2}s^{-1}]	1.27×10^{-8}
Partial molar volume V_H [m^{3}mol^{-1}]	2.0×10^{-6}
Trap binding energy W_B [Jmol^{-1}]	-60×10^3

Table 2 Dimensions of two kinds of model used in the analysis

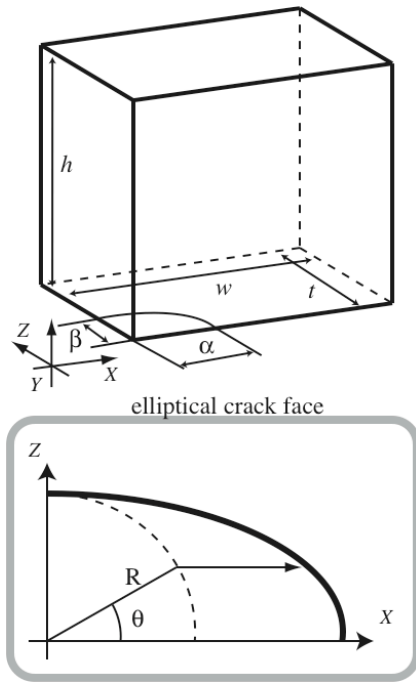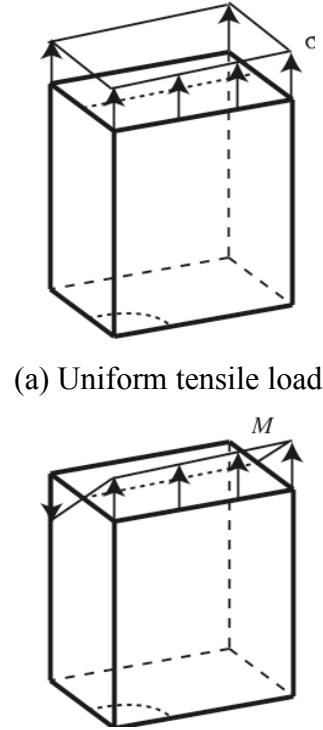|	
α	1, 2, 3, 4
β	1
w	8
t	2.5
h	6

Unit : mm

Fig. 1 A quarter of a finite plate with a semi-elliptical surface crack

(a) Uniform tensile load

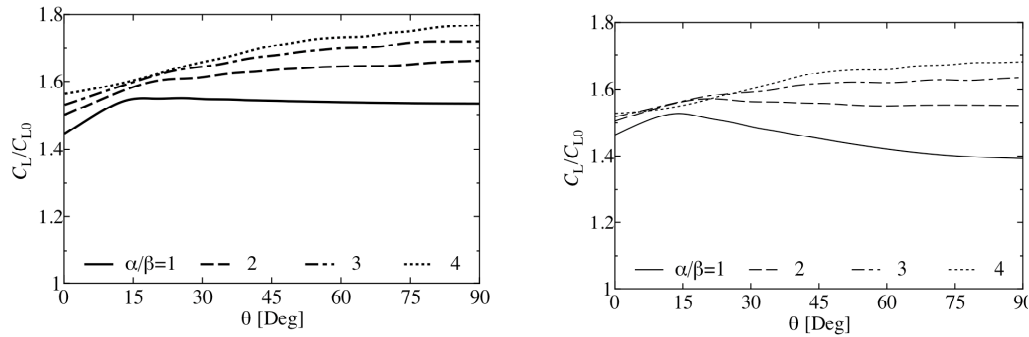(b) Uniform bending moment
Fig. 2 Two kinds of load

of 200MPa was applied to the end of the plate in the latter case. Loading is increased linearly with time until it reaches the maximum value, and the loading time t_{Load} is defined as the time required for reaching the maximum load. t_{Load} was equal to 100 seconds for all analyses in the present study. We also assumed that the initial hydrogen concentration C_{L0} and the initial radius of the bluntingcrack tip b_0 are respectively 1 mass ppm and 5μm. As a boundary condition for a hydrogen diffusion analysis, we considered zero hydrogen flux, that is, $\phi = \mathbf{J} \cdot \mathbf{n} = 0$, on all boundaries including plate surfaces and the crack surfaces. We have to employ an adequate finite element model, because a large amount of computational time is required to obtain the transient solution of a nonlinear three-dimensional finite element analysis. Based on the preliminiminary analysis, in which the number of finite elements were changed, we determined the finite element model used in the analysis. As a result, we used finite element model consisting of 9,792 eight-noded isoparametric elements with 11,187 nodes, which has the minimum mesh size of 1μm.

4. Results and Discussion

We performed hydrogen diffusion analyses for four cases of crack shape, $\alpha / \beta = 1$, 2, 3 and 4 under both the tensile load and the bending moment. The contours of hydrogen concentration at the lattice sites C_{L} are respectively shown in Figs. 3(a) and 3(b) for the tensile load and for the bending moment in case of the crack
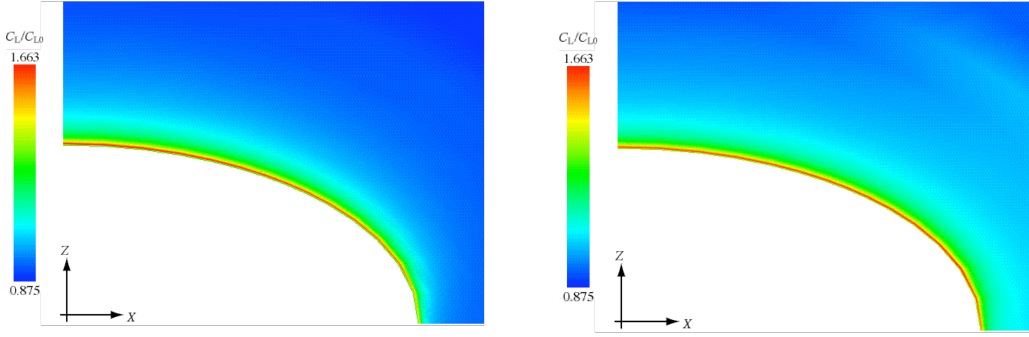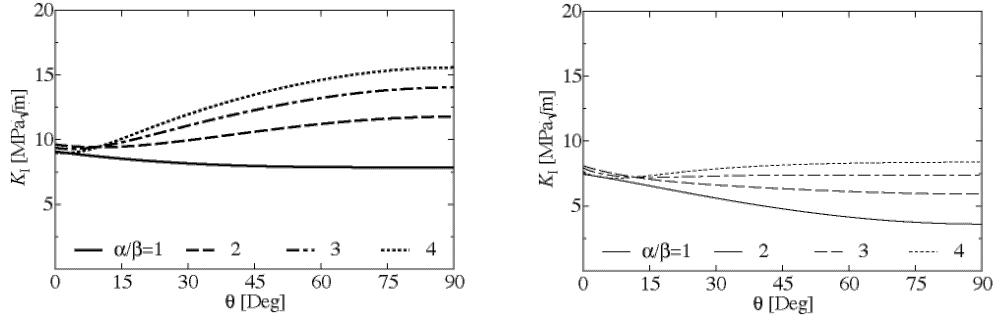
(a) Uniform tensile load   (b) Uniform bending moment

Fig. 3 Contour of hydrogen concentration at the lattice sites

(a) Uniform tensile load   (b) Uniform bending moment

Fig. 4 Distributions of the maximum hydrogen concentration at the lattice sites
along the elliptic angle

shape with α/β =2. For the tensile load, the region with relatively high hydrogen concentration spreads only along the crack front, while, for the bending moment, it spreads not only along the crack front but also along the plate surface. In the latter case, hydrogen moves towards the plate surface due to the stress gradient caused by the bending moment. Figs. 4(a) and 4(b) show the distributions of the maximum hydrogen concentration at the lattice sites C_{L} along the elliptic angle θ defined in Fig. 1 for the tensile load and for the bending moment, respectively. As shown in Fig. 3, the hydrogen concentration has the maximum value at the ligament location very close to the crack front. Figs. 4(a) and 4(b) are obtained by connecting these maximum values along the elliptic angle θ. The results for four cases of the crack shape, α/β =1, 2, 3 and 4, are given in these figures. Now let us pay attention to the hydrogen concentrations at $\theta = 0°$ (the long-axis direction) and 90°(the short-axis direction). For the tensile load, the hydrogen concentration is higher at $\theta = 90°$ than at $\theta = 0$ for all cases of the crack shape. For the bending moment, the hydrogen concentration is higher at $\theta = 90°$ than at $\theta = 0$ for the cases of the crack shape with α/β =2, 3 and 4, but it is vice versa for the case of a semi-circular crack (α/β =1).

(a) Uniform tensile load   (b) Uniform bending moment

Fig. 5 Distributions of the stress intensity factor calculated from
Newman-Raju solutions

Let us discuss the effect of hydrogen on crack growth behavior under cyclic loading. It is well known that a semi-elliptical surface crack grows in the depth direction or the Z-direction in Fig. 1 under a cyclic uniform tensile load and grows in the surface direction or the X-direction under a cyclic bending moment. These crack growth behavior can be explained by the distribution of the stress intensity factor along the crack front. For the stress intensity factors of semi-elliptical surface cracks, we can use so-called Newman-Raju solutions [18]. Figs. 5(a) and 5(b) show the distributions of the stress intensity factor along the crack front obtained from Newman-Raju solutions for the tensile load and for the bending moment, respectively. When the cyclic tensile load is applied, the stress intensity factor is larger at $\theta = 90°$ than at $\theta = 0°$ for a semi-elliptical surface crack with a flat shape (α/β =2, 3 and 4), so that it grows faster in the depth direction than in the surface direction, and it tends to become a semi-circular shape. If we consider the distributions of hydrogen concentration given in Fig. 4(a), the crack growth rate in the depth direction is expected to be more accelerated than that in the surface direction, because the acceleration of crack growth rate due to hydrogen was observed in the fatigue tests using hydrogen charged specimens [1]. When the cyclic bending moment is applied, the stress intensity factor is smaller at $\theta = 90°$ than at $\theta = 0°$ for a semi-circular surface crack (α/β =1) and a semi-elliptical surface crack with a relatively small value of α/β (α/β =2), so that it grows faster in the surface direction than in the depth direction, and it tends to become a flat shape. Considering the distributions of hydrogen concentration given in Fig. 4(b), the acceleration of crack growth in the surface direction is expected in earlier stage because of higher hydrogen concentration at $\theta = 0$ than at $\theta = 90$ in earlier stage, then such effect is decreased, and finally the acceleration of crack growth in the depth direction is expected.

We have to check the LBB (=leak-before-break) concept for pressure vessels and piping to ensure their structural integrity. How does hydrogen affect the LBB for such components? We can derive the answer from the above discussion as follows. Although crack growth rate is enhanced by hydrogen, the flatness of a surface crack that results in the possibility of break before leak does not seem to be

enhanced by hydrogen. It is therefore concluded that hydrogen does not have harmful effect on the LBB.

5. Concluding Remarks

In the present paper, we developed a three-dimensional computer program for a transient hydrogen diffusion analysis. Using the computer program developed in the present study, we performed transient diffusion analyses of a surface crack in a finite plate under tension or bending, and clarified the hydrogen concentration around the periphery of a surface crack. We also made a discussion on the effect of hydrogen on the crack growth behavior under cyclic loading. As a result, it is concluded that hydrogen does not have harmful effect on the leak-before-break.

References

[1] Y. Murakami, The effect of hydrogen on fatigue properties of metals used for fuel cell system, Int J Fract 138 (2006) 167-195.

[2] E.A.Steigerwald, F.W. Schaller, A.R. Troiano, The role of stress in hydrogen induced delayed failure, Trans Am Inst Mining Metall Engineers 218 (1960) 832-841.

[3] R.A. Oriani, P.H. Josephic, Equilibrium aspects of hydrogen-induced cracking of steels, Acta Metall 22 (1974) 1065-1069.

[4] C.D. Beachem, A new model for hydrogen-assisted cracking (Hydrogen "embrittlement"), Metal Trans 3 (1972) 437-451.

[5] A.T. Yokobori Jr., T. Nemoto, K. Satoh, T. Yamada, Numerical analysis on hydrogen diffusion and concentration in solid with emission around the crack tip, Engng Fract Mech 55 (1996) 47-60.

[6] P. Sofronis, R.M. McMeeking, Numerical analysis of hydrogen transport near a blunting crack tip, J Mech Phys Solids 37 (1989) 317-350.

[7] A.H.M. Krom, R.W.J. Koers, A. Bakker, Hydrogen transport near a blunting crack tip, J Mech Phys Solids 47 (1999) 971-992.

[8] P. Sofronis, Y. Liang, N. Aravas, Hydrogen induced shear localization of the plastic flow in metals and alloys, Eur J Mech A/Solids 20 (2001) 857-872.

[9] A. Kimura, H. Matsui, H. Kimura, The work-hardening behavior of hydrogen-charged high-purity iron single-crystals at temperatures between 296-K and 200-K, Mat Sci Engng 58 (1983) 211-222.

[10] A. Taha, P. Sofronis, A micromechanics approach to the study of hydrogen transport and embrittlement, Engng Fract Mech 6 (2001) 803-834.

[11] Y. Liang, P. Sofronis, Toward a phenomenological description of hydrogen induced decohesion at particle/matrix interface, J Mech Phys Solids 51 (2003) 1509-1522.

[12] A.T. Yokobori Jr, T. Uesugi, M. Sendoh, M. Shibata, The effect of stress wave form on corrosion fatigue crack growth rate on the basis of hydrogen diffusion theory, Strength Fract and Complexity 1 (2003) 187-204.

[13] H. Kotake, R. Matsumoto, S. Taketomi, N. Miyazaki, Transient hydrogen diffusion analyses coupled with crack-tip plasticity under cyclic loading, Int J Pressure Vessels and Piping 85 (2008) 540-549.

[14] A.J. Kumnick, H.H. Johnson, Deep trapping states for hydrogen in deformed iron, Acta Metall 28 (1980) 33-36.

[15] R.A. Oriani, P.H. Josephic, Equilibrium aspects of hydrogen-induced cracking of steels, Acta Metall 22 (1974) 1065-1069.

[16] Y. Fukai, H. Sugimoto, Diffusion of hydrogen in metals, Advances in Physics 34 (1985) 263-326.

[17] H. Kanayama, M. Ogino, R. Miresmaeili, T. Nakagawa, T. Toda, Hydrogen Transport in a Coupled Elastoplastic-Diffusion Analysis near a Blunting Crack Tip 2 (2008) 499-510.

[18] J.C. Newman Jr, I.S. Raju, Analyses of surface cracks in finite plates under tension or bending loads, NASA Technical Paper 1578 (1979).