



THE INFLUENCE OF MOBILITY OF DISSOLVED HYDROGEN ON THE ELASTIC RESPONSE OF A METAL

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ABSTRACT

The general principles of the mechanics of materials are used to describe the effect of interstitial mobile hydrogen on the linear elastic behavior of metals and alloys. The linear field equations reveal that during transient hydrogen diffusion the Laplacian of the hydrostatic stress is related to the Laplacian of the hydrogen concentration in the lattice, and it is not zero, as has often been assumed in calculations involving stress-driven diffusion of hydrogen under plane strain conditions. When the hydrogen reaches equilibrium with the local stress and diffusion terminates, the linear elastic constitutive response of the solid accounting for the hydrogen effect can be described by the standard Hooke's law of infinitesimal elasticity in which the stiffness moduli are termed moduli at fixed solute chemical potential and are calculated in terms of the moduli at fixed solute composition, the nominal hydrogen concentration, and the material parameters of the system. These moduli at fixed solute chemical potential can be viewed as the counterparts of those characterizing the drained deformation at constant pressure of fluid-infiltrated porous geomaterials, or the adiabatic deformation of thermoelastic materials. Next the linear transient field equations are solved in the case of a dislocation and a line force in an infinite medium under plane strain conditions by using analytic function theory. The range of validity of the solution to the linear field equations for an isolated edge dislocation is investigated for specific materials. Lastly, the implications of the constitutive behavior of the hydrogen-metal binary system on the fracture and dislocation behavior are discussed when the hydrogen is in equilibrium with local stress.

1. INTRODUCTION

The interaction of hydrogen with elastic deformation is a result of the lattice dilatation caused by hydrogen in solid solution with a metal or alloy. The study of this interaction recently (Sirois *et al.*, 1992; Birnbaum and Sofronis, 1994; Sofronis and Birnbaum, 1995) has increased significantly the understanding of the macroscopic mechanical behavior of materials in the presence of hydrogen.

Hydrogen transport through the lattice is considered to be a significant component of the overall hydrogen degradation mechanism (Hirth, 1980). The general thermomechanical theory of a diffusing and chemically reacting mixture of elastic materials has been successfully formulated from a continuum mechanics viewpoint by Bowen (1967, 1976) and by Bowen and Wiese (1969). An application of the theory is the extension of the pioneering work of Biot (1941, 1955, 1956, 1973) in the description of the constitutive and field equations for porous media (Bowen, 1982).

Motivated by the approach of the theory of mixtures, Aifantis (1980) modeled the phenomenological aspects of diffusion in solids on the basis of the physical principle of conservation of momentum. Rice and Cleary (1976) modeled the elastic behavior of fluid-infiltrated porous geomaterials and developed an elegant theory with direct physical interpretation and an associated problem solution methodology. Following Rice and Cleary's (1976) formalism, McTigue (1986) provided a description of the thermoelastic response of fluid-saturated porous rock. Larche and Cahn (1985) investigated the interaction of solute composition and stress in crystalline solids and studied the effect of this interaction on several physical phenomena, such as the formation of an atmosphere around a dislocation, vacancy equilibrium and diffusional creep.

In most work to date, solutions for the hydrogen transport problem in an elastically-deforming material were obtained, at least in the more sophisticated treatments, through a nonlinear equation for stress-driven diffusion coupled with the linear elastic deformation of the lattice which, though, was treated as unaffected by hydrogen (Liu, 1970; Van Leeuwen, 1974; Dutton *et al.*, 1977). In addition, the study of the transient hydrogen diffusion under plane strain elastic deformation was carried out on the basis that the term involving the Laplacian of the hydrostatic stress can be dropped from the diffusion equation accounting for drift. In a linear theory this is true only at the beginning when the concentration is uniform throughout the solid, and in the end when diffusion terminates and hydrogen reaches equilibrium with local stress. During transient hydrogen diffusion, total strain compatibility dictates a relationship between the local hydrostatic stress which is associated with the elastic dilatation and the hydrogen concentration which is directly related to the hydrogen-induced strain in the lattice. As will be seen in Section 3 the contribution of the term associated with the Laplacian of the hydrostatic term to the time rate of change of the hydrogen concentration can be comparable in magnitude to that arising from the gradients of the concentration.

The purpose of this article is to state a constitutive model for the linear behavior of the composite system made of a metal or alloy and interstitial hydrogen in solid solution. In particular, the aim is to derive a linear equation for the transient stress-driven hydrogen diffusion coupled with the linear elastic deformation of the solid accounting for the hydrogen-induced strains. The development of the model follows the work of Rice and Cleary (1976) for fluid-saturated porous elastic solids. In Section 2, the linear elasticity theory is used to describe the infinitesimal deformation of a solid containing mobile interstitial atoms in solution. In Section 3, the equations are specialized for the isotropic material containing interstitial hydrogen in solution and, as an application, the moduli at fixed solute chemical potential are evaluated for the H/Ta, H/Nb and H/V systems at room temperature as functions of the nominal hydrogen concentration. In Section 4, linear elasticity is used to set up and solve the boundary value problem for an edge dislocation and a line force in an infinite medium under plane strain conditions. As an application, the transient hydrogen concentration and stress fields for an isolated edge dislocation are obtained. The implications of the theory for understanding the hydrogen effect on dislocation plasticity and the hydrogen-induced fracture in metals and alloys are discussed in Section 5.

From now on, Cartesian vectors and tensors are denoted by bold-face roman letters (**A**, **a**) and their scalar components by the corresponding italic letters (A_{ij} , a_i). When

upper- or lower-case letters are used as indices, they are understood generally to range over 1, 2, and 3. Repetition of any subscript implies summation over the range.

2. LINEAR ELASTICITY OF THE INTERSTITIAL SOLUTE ATOM–METAL BINARY SYSTEM

The interstitial solute atoms are considered to be mobile so that they can flow into or out of any part of the body which is at temperature T , uniform throughout. The stress-free solid at nominal solute concentration, C_0 , is taken as the reference state for measuring strain. The deformation of the body is assumed to be small with infinitesimal strains and the material constitutive response is modeled as linearly elastic. The mechanical effect of an interstitial solute atom is modeled by a strain ϵ^H , linear in solute concentration change, with components given by

$$\epsilon_{ij}^H = H_{ij}(C - C_0), \quad (1)$$

where C denotes the concentration of the solute atoms measured in atoms per unit lattice volume and H_{ij} denotes strain brought about by a solute concentration change of one atom per unit lattice volume in the absence of any stress. In general, strain ϵ^H may contain both dilatational and shear components. In the case of the hydrogen binary systems, the strain, ϵ^H , is experimentally observed to be purely dilatational. In addition the parameter H_{ij} is approximately constant, independent of the solute concentration even for concentration levels, measured in hydrogen atoms per metal atom (H/M), of order close to unity (Peisl, 1978). Under the action of external loads which cause local stress, σ , the components of the total strain

$$\epsilon_{ij} = (u_{i,j} + u_{j,i})/2, \quad (2)$$

where u_i is the displacement and $(\)_{,i} = \partial(\)/\partial x_i$, are given by

$$\epsilon_{ij} = K_{ijkl}\sigma_{kl} + H_{ij}(C - C_0), \quad (3)$$

where \mathbf{K} is the linear elastic compliance tensor at nominal solute concentration C_0 . Total strain ϵ_{ij} obeys the compatibility condition (Sokolnikoff, 1956)

$$\epsilon_{ij,kl} + \epsilon_{kl,ij} - \epsilon_{ik,jl} - \epsilon_{jl,ik} = 0, \quad (4)$$

and stress σ_{ij} satisfies the equilibrium equations

$$\sigma_{ij,j} = 0 \quad (5)$$

in the absence of body forces.

The chemical potential, μ , of a mobile interstitial solute atom at any position within the elastically-stressed solid is defined to be the isothermal reversible work required to introduce the atom at that location from a chemical reservoir at the same temperature with the body and hydrogen pressure p , while the displacements are held fixed on the loaded external boundary. Neglecting the strain energy change of the stressed solid due to the addition of an extra atom to it (Li *et al.*, 1966; Rice and

Chuang, 1981), one can express the chemical potential of the solute atom as (Li *et al.*, 1966; Larche and Cahn, 1985)

$$\mu(\sigma_{ij}, T, C) = \mu_0 + kT \ln \left(\frac{C}{C_0} \right) - H_{ij} \sigma_{ij} - p H_{kk}, \quad (6)$$

where μ_0 is the chemical potential of an atom in the reservoir at the same pressure and at a solute concentration equal to the nominal, C_0 , and k is Boltzmann's constant. Chemical potential gradients motivate diffusive flux of the mobile interstitial atoms which in the case of low concentrations, at which there is no interaction between the diffusing atoms, is described phenomenologically by Fick's first law

$$\mathbf{j} = - \frac{DC}{kT} \nabla \mu, \quad (7)$$

where \mathbf{j} denotes the flux vector, D is the positive lattice diffusion constant measured in area per unit time and assumed to be independent of stress and concentration, and ∇ denotes the gradient operator. The amount of atoms that flows in the sense of the unit vector \mathbf{n} across a surface normal to \mathbf{n} per unit area per unit time is $j_i n_i$. The use of a scalar diffusion constant in (7) is valid only for crystalline solids whose lattice has cubic symmetry.

Using (6), (7) and Fick's second law for diffusion one obtains the governing equation for the isothermal diffusion of interstitial solute atoms that accounts for drift due to stress. The linearized form of this equation is written as

$$\frac{\partial C}{\partial t} = D \nabla^2 C - \frac{DC_0}{kT} H_{ij} \nabla^2 \sigma_{ij}, \quad (8)$$

where $\partial/\partial t$ denotes differentiation with respect to time and ∇^2 stands for the Laplacian, $\nabla^2(\cdot) = (\cdot)_{,ii}$.

At times much greater than the characteristic diffusion time of the system the gradients in the local chemical potential of the interstitial solute atoms are neutralized and diffusion terminates. Integration of the linearized zero flux condition, $-D \nabla C + DC_0 \nabla (H_{ij} \sigma_{ij}) / kT = 0$, yields the solute atom concentration, C , in equilibrium with local stress as

$$C - C_0 = \frac{H_{ij} \sigma_{ij}}{kT} C_0, \quad (9)$$

where the nominal concentration C_0 at zero stress is used as boundary condition. In that case the constitutive equation (3) can be written with use of (9) solely in terms of the compliance tensor at fixed solute chemical potential, \mathbf{K}^μ , as

$$\varepsilon_{ij} = K_{ijkl}^\mu \sigma_{kl}, \quad (10)$$

where

$$K_{ijkl}^\mu = K_{ijkl} + C_0 \frac{H_{ij} H_{kl}}{kT}. \quad (11)$$

According to (11) the moduli at fixed solute chemical potential are evaluated in terms of the nominal hydrogen concentration C_0 about which the linear field equations have been written down. For a system that is in contact with a chemical reservoir, the composition at equilibrium under zero stress is usually a good choice for a nominal concentration, as Larche and Cahn (1985) maintain, since it constitutes the physical basis for stating the linear field equations.

Notice the direct analogy between the coupled diffusion and deformation in fluid-infiltrated geomaterials (Rice and Cleary, 1976) and the response under stress of a solid solution system whose interstitial solute atoms are mobile and can diffuse through the lattice. The undrained deformation and the associated undrained moduli at constant fluid mass content m correspond to the deformation at constant solute atom concentration C_0 and the related moduli \mathbf{K} defined by (3) at fixed solute composition. In both fluid-infiltrated and interstitial solute atom-containing solids the conditions for undrained deformation and deformation at fixed solute composition, respectively, are obtained during fast straining. Drained deformation at constant pore pressure p and the related drained moduli correspond to equilibrium situations at fixed solute chemical potential μ and the associated moduli defined by (11). Both drained and fixed solute chemical potential deformations are the case when the straining is slow. Similarly the elastic moduli at fixed solute chemical potential can be viewed as counterparts of the adiabatic elastic moduli which characterize the adiabatic straining of a thermoelastic material.

3. LINEAR ISOTROPIC ELASTICITY OF THE INTERSTITIAL HYDROGEN SOLUTE ATOM-METAL BINARY SYSTEM

The solution of hydrogen into a stress-free metal lattice is characterized by a volume dilatation Δv of the host lattice per hydrogen atom (Peisl, 1978; Hirth, 1980). Volume change Δv is directly related to the partial molar volume of hydrogen in solution, V_H , through $V_H = \Delta v N_A$, where N_A is Avogadro's number. Hence one may write the local unconstrained volume dilatation of the lattice (Peisl, 1978) as

$$e^H = (c - c_0) \frac{\Delta v}{\Omega}, \quad (12)$$

where c is the hydrogen concentration measured in hydrogen atoms per host lattice atom and $\Omega = V_M/N_A$ is the mean atomic volume of the host lattice with molar volume V_M . For dilute solutions, i.e. for $c, c_0 \ll 1$,

$$C = \frac{c}{\Omega}, \quad (13)$$

and setting

$$\lambda = \frac{\Delta v}{\Omega}, \quad (14)$$

one may write the local hydrogen-induced strain at zero stress as

$$\varepsilon_{ij}^H = \frac{1}{3}\lambda\Omega(C - C_0)\delta_{ij}. \quad (15)$$

Strain tensor ε^H is often referred to as the hydrogen-induced transformation strain in the treatment of the hydrogen mechanical effect (Sofronis and Birnbaum, 1995). Comparison of (1) and (15) yields

$$H_{ij} = \frac{1}{3}\lambda\Omega\delta_{ij} \quad (16)$$

for the hydrogen-metal system and upon substitution into (3)

$$\varepsilon_{ij} = K_{ijkl}\sigma_{kl} + \frac{1}{3}\lambda\Omega(C - C_0)\delta_{ij}. \quad (17)$$

For isotropic material (17) becomes

$$\varepsilon_{ij} = \frac{1+\nu}{E}\sigma_{ij} - \frac{\nu}{E}\sigma_{kk}\delta_{ij} + \frac{1}{3}\lambda\Omega(C - C_0)\delta_{ij}, \quad (18)$$

where E is the Young's modulus and ν is the Poisson's ratio at fixed solute composition C_0 and zero external applied load. Inserting (18) into the compatibility condition (Sokolnikoff, 1956)

$$\varepsilon_{ij,kl} + \varepsilon_{kl,ij} - \varepsilon_{ik,jl} - \varepsilon_{jl,ik} = 0 \quad (19)$$

and using the equilibrium condition (5), one obtains six independent compatibility equations which can be written in terms of σ_{ij} and C as

$$\sigma_{ij,kk} + \frac{1}{1+\nu}\sigma_{mm,ij} = -\frac{1}{3}\lambda\Omega\left(\frac{E}{1+\nu}C_{,ij} + \frac{E}{1-\nu}C_{,kk}\delta_{ij}\right). \quad (20)$$

Contraction on i, j results in a relationship between the Laplacian of the hydrostatic stress σ_{kk} and the Laplacian of the hydrogen concentration C :

$$\nabla^2\sigma_{kk} = -\frac{2}{3}\frac{E}{1-\nu}\lambda\Omega\nabla^2C. \quad (21)$$

Substituting (16) into (8), and replacing $\nabla^2\sigma_{kk}$ by ∇^2C from (21), one finds the equation for transient hydrogen diffusion to be

$$\frac{\partial C}{\partial t} = D_{\text{eff}}\nabla^2C, \quad (22)$$

where the effective diffusion constant D_{eff} is given by

$$D_{\text{eff}} = D\left(1 + \frac{2}{9}\frac{C_0}{kT}\frac{E}{1-\nu}\lambda^2\Omega^2\right). \quad (23)$$

Next, the Young's modulus E^μ , Poisson's ratio ν^μ , and shear modulus G^μ at fixed solute chemical potential will be evaluated in terms of the corresponding moduli E , ν , and G at fixed solute composition. It has been observed experimentally (Peisl, 1978) that the strain due to hydrogen is purely hydrostatic for crystals of cubic symmetry or for an isotropic solid. Thus any moduli defined in terms of the deviatoric stresses and strains are the same regardless of whether they are defined under fixed solute

composition or fixed solute chemical potential. Hence, for isotropic elasticity of the hydrogen-metal system the shear modulus satisfies

$$G^\mu = G. \quad (24)$$

Combining (11) when the material is isotropic with (16) and (24), one finds

$$E^\mu = \frac{E}{1 + \xi \lambda^2 E}, \quad (25)$$

$$\nu^\mu = \frac{\nu - \xi \lambda^2 E}{1 + \xi \lambda^2 E}, \quad (26)$$

where

$$\xi = \frac{c_0 \Omega}{9kT}. \quad (27)$$

The bulk modulus B^μ at fixed solute chemical potential is then given by

$$\frac{1}{B^\mu} = \frac{1}{B} + 9\xi \lambda^2, \quad (28)$$

where B is the bulk modulus at fixed solute composition. Equation (26) indicates that the Poisson's ratio at fixed solute chemical potential becomes nonpositive when

$$c_0 \geq \frac{9\nu kT}{E\Omega \lambda^2}. \quad (29)$$

Equations (24), (25), (26), and (28) are identical with equations (5.6) in the work of Larche and Cahn (1985).

Inserting (16) into (9) yields the concentration C in equilibrium with the local hydrostatic stress σ_{kk} :

$$C - C_0 = \frac{\lambda \Omega C_0 \sigma_{kk}}{3kT}. \quad (30)$$

When hydrogen reaches equilibrium with local stress and diffusion terminates, (22) implies that $\nabla^2 C = 0$ and hence $\nabla^2 \sigma_{kk} = 0$ by (30). During transient hydrogen diffusion the contribution from the term associated with the Laplacian $\nabla^2 \sigma_{kk}$ to the time rate of change of the concentration C is reflected in the effective diffusion constant, D_{eff} . Neglect of this contribution may result in an error that scales directly with the ratio $(D_{\text{eff}} - D)/D$ which at room temperature, as can be deduced from Fig. 1 for typical metals and nominal concentrations less than 0.1 H/M, may vary between 0 and 0.6 depending upon the nominal concentration.

Using (25), (26), (27), and (13), one may write (23) for the effective diffusion constant in terms of the Poisson's ratios at fixed solute composition and chemical potential as

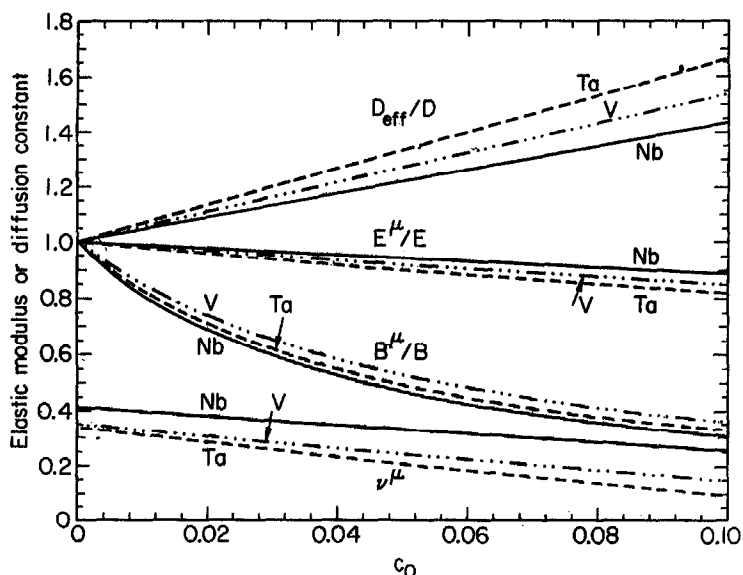


Fig. 1. Plot of Young's modulus E^μ/E , Bulk modulus B^μ/B and Poisson's ratio ν^μ at fixed solute chemical potential; and of effective diffusion constant D_{eff}/D versus nominal hydrogen concentration c_0 in the Ta/H, Nb/H and V/H systems at temperature 300 K. Nominal concentration c_0 is measured in hydrogen atoms per metal atom. Constants E , and B , are Young's and Bulk modulus for the hydrogen-free material, respectively, and D is the normal lattice diffusion constant.

$$D_{\text{eff}} = D \frac{(1 + \nu)(1 - \nu^\mu)}{(1 - \nu)(1 + \nu^\mu)}. \quad (31)$$

Equations (22) and (31) describe the transient hydrogen diffusion motivated by stress and concentration gradients at given nominal concentration C_0 . The stress effect has been absorbed into the effective diffusion constant, D_{eff} , and therefore, existing solutions for hydrogen transient diffusion according to Fick's second law can be used in which the normal lattice diffusion constant, D , is replaced by D_{eff} . Consequently, the linear isotropic elasticity of the hydrogen-metal system is uncoupled in the sense that the solution for the hydrogen concentration can be found directly in terms of the diffusion constant D and the Poisson's ratios ν and ν^μ which are all known prior to the calculation of the stress field. Then at a given time, after the corresponding hydrogen concentration field has been calculated and the constitutive behavior of the material lattice is completely characterized through (18), one can solve the elasticity boundary value problem, as governed by (2), (5) and (18), for the calculation of stress and strain. In particular, when the concentration of hydrogen solutes reaches equilibrium with local stress, the corresponding local hydrostatic stress can be calculated directly from (30) without first solving the elasticity boundary value problem. Of course, for the linear equations to continue to be valid as the time elapses, the calculated concentration field, C , should not be much different from the nominal concentration field C_0 . An investigation of the conditions at which the linearity

assumption breaks down is given in the edge dislocation problem studied in Subsection 4.3.

3.1. Application: H/Ta , H/Nb , H/V and H/Fe systems

The Young's modulus and Poisson's ratio for the hydrogen-free material were taken to be the moduli E and ν at fixed solute composition. This approximation can be considered fairly reliable in the case of dilute solutions. Thus, E was taken as equal to 189.3, 87.1, 128.8 and 200 GPa, and ν equal to 0.339, 0.415, 0.352 and 0.300, respectively, for Ta, Nb, V and Fe. The data for the Nb system are from the work of Mazzolai and Birnbaum (1985a, b); those for Ta and V are from Hirth and Lothe (1982); and those for Fe from Boyer and Gall (1985). The atomic volume Ω for Ta, Nb and V was calculated $0.18 \times 10^{-28} \text{ m}^3/\text{atom}$ from the lattice parameter $a = 3.301 \text{ \AA}$, and that for Fe was calculated $0.12 \times 10^{-28} \text{ m}^3/\text{atom}$ from the magnitude of $a = 2.887 \text{ \AA}$ (Boyer and Gall, 1985). The ratio of volume expansion per hydrogen atom to volume of the host lattice atom is $\lambda = 0.155, 0.174$ and 0.190 correspondingly for the H/Ta , H/Nb and H/V systems (Peisl, 1978); and $\lambda = 0.276$ for the Fe/H system a value which corresponds to a partial molar volume of hydrogen in solution of $2 \text{ cm}^3/\text{mole}$ (Hirth, 1980).

In Fig. 1, Young's modulus E^μ , Poisson's ratio ν^μ and bulk modulus B^μ at fixed solute chemical potential, as given by (25), (26) and (28), respectively, are plotted against nominal hydrogen concentration c_0 for the H/Ta , H/Nb and H/V systems at $T = 300 \text{ K}$. In the same figure the effective diffusion constant D_{eff} as given by (31) is plotted too. The elastic moduli E^μ , B^μ are normalized respectively by the moduli E , B for the hydrogen-free material and the effective diffusion constant, D_{eff} , is normalized by the normal lattice diffusion constant D . The ratio D_{eff}/D is greater than unity because of the stress effect on the diffusion of hydrogen. The moduli E^μ , ν^μ , B^μ decrease with hydrogen concentration and the implications of this behavior to the dislocation plasticity and fracture of the materials are discussed in Section 5. The minimum nominal concentration c_0 at which the parameter ν^μ becomes negative at temperature 300 K is calculated from (29) to be $0.154, 0.326, 0.201$ and 0.061 for solute hydrogen in Ta, Nb, V and Fe, respectively. Therefore, a negative Poisson's ratio at fixed solute chemical potential may, indeed, be the case in the H/Ta , H/Nb and H/V systems, but it is practically impossible for the H/Fe system in which the hydrogen solubility is very small, that is, of the order of four hydrogen atoms per 10^8 Fe atoms in equilibrium with gas at one atmosphere pressure (Johnson, 1974).

4. SINGULAR SOLUTION FOR EDGE DISLOCATION AND LINE FORCE

4.1. Governing equations for plane strain deformation

Throughout this section Greek indices are used for the range 1, 2 and a repeated Greek index implies summation over the range. In plane strain deformation, parallel to the x_1, x_2 -plane, the component u_3 of the displacement vector vanishes and the components u_1 and u_2 are functions of the coordinates x_1 and x_2 but not of x_3 . As a

result, the kinematic constraint $\varepsilon_{3j} = 0$ in conjunction with constitutive equation (18) requires

$$\sigma_{33} = \nu\sigma_{\gamma\gamma} - \frac{E}{3}\lambda\Omega(C - C_0), \quad \sigma_{31} = \sigma_{32} = 0, \quad (32)$$

and hence

$$\sigma_{kk} = (\nu + 1)\sigma_{\gamma\gamma} - \frac{E}{3}\lambda\Omega(C - C_0). \quad (33)$$

Then, the constitutive equation (18) can be written as

$$2G\varepsilon_{\alpha\beta} = \sigma_{\alpha\beta} - \nu\sigma_{\gamma\gamma}\delta_{\alpha\beta} + \frac{E}{3}\lambda\Omega(C - C_0)\delta_{\alpha\beta}. \quad (34)$$

Equilibrium equations (5) are written as

$$\sigma_{11,1} + \sigma_{12,2} = 0, \quad (35)$$

$$\sigma_{12,1} + \sigma_{22,2} = 0, \quad (36)$$

and with use of (33) for the hydrostatic stress the compatibility condition becomes

$$\nabla^2\sigma_{\gamma\gamma} = -\frac{E}{3(1-\nu)}\lambda\Omega\nabla^2C. \quad (37)$$

Lastly combining (30), (25), (26), and (27), one finds that when hydrogen reaches equilibrium with local stress, a condition which is always attained as time $t \rightarrow \infty$, the in-plane hydrostatic stress $\sigma_{\gamma\gamma}$ is related to the corresponding equilibrium concentration by

$$\sigma_{\gamma\gamma} = \frac{E}{3(\nu - \nu^\mu)}\lambda\Omega(C - C_0). \quad (38)$$

If σ_{11} , σ_{22} , σ_{12} , and C are chosen as the independent field variables the governing equations are described by the set of equations (32) through (37) along with the transient diffusion equation (22) which, as was discussed in Section 3, can be solved directly under appropriate boundary and initial conditions.

In order to solve for the stresses σ_{11} , σ_{22} and σ_{12} , following Rice and Cleary (1976) one may define

$$4 \operatorname{Re} [\Phi(z, t)] = \sigma_{\gamma\gamma} + \frac{E}{3(1-\nu)}\lambda\Omega(C - C_0), \quad (39)$$

where $\Phi(z, t)$ is an analytic complex function of the complex variable $z = x_1 + ix_2$ with $i = \sqrt{-1}$; Re means "real part of", and as is indicated by (39) the function $\Phi(z, t)$ is in general time dependent. It may be assumed that immediately after the introduction of the edge dislocation into the perfect crystal ($t = 0^+$) the classical elasticity solution based on the moduli ν , E and G at fixed solute composition C_0 applies. Similarly, the classical elasticity solution based on the moduli ν^μ , E^μ and G^μ

at fixed solute chemical potential applies when diffusion terminates ($t \rightarrow \infty$). Therefore (39) yields

$$(\sigma_{\gamma\gamma})_{0^+} = 4 \operatorname{Re} [\Phi(z, 0^+)], \quad (40)$$

and in conjunction with (38)

$$(\sigma_{\gamma\gamma})_{\infty} = 4 \frac{1-\nu}{1-\nu^e} \operatorname{Re} [\Phi(z, \infty)]. \quad (41)$$

If the function $\Phi(z, t)$ is time independent it should satisfy $\Phi(z, 0^+) = \Phi(z, \infty)$. In that case (40) and (41) indicate that traction boundary value problems are excluded since in these problems the solution for the stresses does not depend on the elastic moduli. Furthermore, (40) and (41) indicate that in order for $\Phi(z, 0^+) = \Phi(z, \infty)$ the solution for $\sigma_{\gamma\gamma}$ should be inversely proportional to a factor $1-\nu^e$ so that

$$\sigma_{\gamma\gamma} = 4 \frac{1-\nu}{1-\nu^e} \operatorname{Re} [\Phi(z, t)], \quad (42)$$

where ν^e is an effective Poisson's ratio such that $\nu^e = \nu$ at $t = 0^+$ and $\nu^e = \nu^\mu$ at $t \rightarrow \infty$. This is, as Rice and Cleary (1976) observe, exactly the feature of some basic singular elasticity solutions, such as the classical plane strain solutions for an isolated edge dislocation and an isolated line force, which has led us to extract their counterparts in linear isotropic elasticity of the hydrogen-metal system.

4.2. Plane strain solution in terms of complex potentials

Following the corresponding formalism in classical elasticity (Muskhelishvili, 1953), one can express the solution to the plane strain governing equations for the stresses and displacements in terms of two analytic functions, complex potentials $\Phi(z, t)$ and $\Psi(z, t)$ of the complex variable $z = x_1 + ix_2$. By considering z and its complex conjugate $\bar{z} = x_1 - ix_2$ as the pair of independent variables, one may write the hydrogen concentration $C(x_1, x_2, t)$, which is not an analytic function, as $C(z, \bar{z}, t)$. By setting

$$\sigma = \frac{\sigma_{11} + \sigma_{22}}{2} \quad \text{and} \quad \tau = \frac{\sigma_{22} - \sigma_{11}}{2} + i\sigma_{12}, \quad (43)$$

equilibrium equations (35) and (36) become

$$\frac{\partial \tau}{\partial \bar{z}} = \frac{\partial \sigma}{\partial z}. \quad (44)$$

By (39) and (43)

$$\sigma = 2 \operatorname{Re} [\Phi(z, t)] - \frac{E}{6(1-\nu)} \lambda \Omega (C(z, \bar{z}, t) - C_0), \quad (45)$$

and upon differentiation

$$\frac{\partial \sigma}{\partial z} = \frac{\partial \Phi(z, t)}{\partial z} - \frac{E}{6(1-\nu)} \lambda \Omega \frac{\partial (C(z, \bar{z}, t) - C_0)}{\partial z}. \quad (46)$$

Inserting this result into (44) and integrating yields

$$\tau = \bar{z} \frac{\partial \Phi(z, t)}{\partial z} + \Psi(z, t) - \frac{E}{6(1-\nu)} \lambda \Omega \int_{f(z, t)}^z \frac{\partial [C(z, \zeta, t) - C_0]}{\partial z} d\zeta, \quad (47)$$

where the lower limit of integration $f(z, t)$ is an arbitrary analytic function to be chosen accordingly with the boundary conditions of the problem, and the analytic function $\Psi(z, t)$ is an arbitrary function of integration.

The expressions for the displacements u_1 and u_2 are obtained as follows. Constitutive equations (34) combined with (43) yield

$$\frac{\varepsilon_{11} + \varepsilon_{22}}{2} = \frac{1}{2G} \left[(1-2\nu)\sigma + \frac{E}{3} \lambda \Omega (C - C_0) \right], \quad (48)$$

$$\frac{\varepsilon_{22} - \varepsilon_{11}}{2} + i\varepsilon_{12} = \frac{\tau}{2G}. \quad (49)$$

Using the strain-displacement relation (2), one can easily show that

$$\frac{\varepsilon_{11} + \varepsilon_{22}}{2} = \operatorname{Re} \left[\frac{\partial (u_1 - iu_2)}{\partial \bar{z}} \right], \quad (50)$$

$$\frac{\varepsilon_{22} - \varepsilon_{11}}{2} + i\varepsilon_{12} = - \frac{\partial (u_1 - iu_2)}{\partial z}. \quad (51)$$

Inserting (45) and (47) into (48) and (49) respectively and combining the result with (50) and (51), one finds by integration that

$$2\mu(u_1 - iu_2) = (3-4\nu)\bar{\varphi}(\bar{z}, t) - \bar{z}\Phi(z, t) - \psi(z, t) + \frac{E}{6(1-\nu)} \lambda \Omega \int_{f(z, t)}^z [C(z, \zeta, t) - C_0] d\zeta, \quad (52)$$

where

$$\frac{\partial \varphi(z, t)}{\partial z} = \Phi(z, t) \quad (53)$$

and

$$\frac{\partial \psi(z, t)}{\partial z} = \Psi(z, t) - \frac{E}{6(1-\nu)} \lambda \Omega [C(z, f(z, t), t) - C_0] \frac{\partial f(z, t)}{\partial z}. \quad (54)$$

The resultant force $F_1 + iF_2$ exerted through any segment of a contour in the x_1, x_2 -plane, where the end points are defined by arclength s_0 and s measured from an arbitrary point on the contour, can be found by integrating the traction vector $T_1 + iT_2$. Thus

$$-i(F_1 - iF_2) = -i \int_{s_0}^s (T_1 - iT_2) ds = \int_{s_0}^s (\sigma d\bar{z} + \tau dz). \quad (55)$$

Since the integrand $\sigma d\bar{z} + \tau dz$ is a perfect differential, the integral of (55) can be calculated in any simply connected region containing no singularities to be

$$-i(F_1 - iF_2) = \bar{z}\Phi(z, t) + \bar{\varphi}(\bar{z}, t) + \psi(z, t) - \frac{E}{6(1-\nu)} \lambda\Omega \int_{\eta(z, t)}^z [C(z, \varsigma, t) - C_0] d\varsigma. \quad (56)$$

4.3. Edge dislocation and point force

Consider a stress-free infinite solid with a uniform hydrogen composition C_0 . The linear elastic constitutive behavior of the material is characterized by the isotropic moduli E , ν and G at fixed solute concentration C_0 . At time $t = 0$ an edge dislocation with Burgers vector $b = b_1 + ib_2$ is suddenly introduced, but quasi-statically, and a point force $P = P_1 + iP_2$, which also begins to act at the origin at the same time. The dislocation and force are to be maintained at all times $t > 0$. As a result, there exist chemical potential gradients which motivate hydrogen diffusion. Eventually, at $t \rightarrow \infty$, the material is characterized by the moduli E^μ , ν^μ , and $G^\mu = G$ at fixed solute chemical potential and the hydrogen concentration field C assumes its equilibrium with local stress value

$$(C - C_0)_\infty = \frac{12(\nu - \nu^\mu)(1 - \nu)}{E(1 - \nu^\mu)} \frac{1}{\lambda\Omega} \text{Re}[\Phi(z, \infty)], \quad (57)$$

which is found by combining (38) and (41). In these two limit cases, i.e. at $t = 0$ and $t \rightarrow \infty$, the classical elasticity solution applies and the corresponding complex potentials $\Phi(z)$ and $\Psi(z)$ are well known and given by

$$\Phi(z) = \frac{1}{1 - \nu^c} \frac{\mathcal{D}}{z}, \quad (58)$$

$$\Psi(z) = \frac{-2G\bar{b} + (3 - 4\nu^c)i\bar{P}}{8\pi i(1 - \nu^c)} \frac{1}{z}, \quad (59)$$

where

$$\mathcal{D} = \frac{2Gb - iP}{8\pi i}, \quad (60)$$

$\nu^c = \nu$ at $t = 0^+$ and $\nu^c = \nu^\mu$ at $t \rightarrow \infty$. In addition, the in-plane hydrostatic stress in these two limit cases is given by

$$\sigma_{\gamma\gamma} = 4 \frac{\mathcal{D}}{1 - \nu^c} \text{Re} \left[\frac{1}{z} \right]. \quad (61)$$

By comparing (42) and (61), one deduces that at $t = 0^+$ and $t \rightarrow \infty$ the function $\Phi(z, t)$ should be of the form

$$\Phi(z, t) = \frac{1}{1-\nu} \frac{\mathcal{D}}{z}, \quad (62)$$

and therefore condition $\Phi(z, 0^+) = \Phi(z, \infty)$ is satisfied. Next a solution is found which verifies that function $\Phi(z, t)$ is time independent.

Substituting (62) into the boundary condition (57), one finds

$$(C - C_0)_\infty = \frac{6(\nu - \nu^\mu)}{E(1 - \nu^\mu)} \frac{1}{\lambda\Omega} \left(\frac{\mathcal{D}}{z} + \frac{\bar{\mathcal{D}}}{\bar{z}} \right). \quad (63)$$

The solution to the transient hydrogen diffusion equation (22) subject to conditions (63) and

$$(C - C_0)_{0^+} = 0 \quad (64)$$

at $t = 0^+$ is given by

$$C - C_0 = \frac{6(\nu - \nu^\mu)}{E(1 - \nu^\mu)} \frac{1}{\lambda\Omega} \left(\frac{\mathcal{D}}{z} + \frac{\bar{\mathcal{D}}}{\bar{z}} \right) \exp \left(-\frac{z\bar{z}}{4D_{\text{eff}}t} \right). \quad (65)$$

Notice that as the distance from the origin increases the hydrogen concentration C , calculated from (65), tends to the nominal concentration C_0 which prevails far away from the dislocation core where the lattice is essentially unstressed. Solution (65) is compatible with dislocation cores which exhibit an infinite capacity to accommodate hydrogen on the tensile side and an infinite ability of the compressive side to provide hydrogen. The latter implies negative hydrogen concentrations in the region of compressive hydrostatic stress. This result, which is discussed in detail in the next section, is related directly to the linear features of the theory used to characterize the hydrogen diffusion in the vicinity of the dislocation core.

In order to use (52) and (56) the integral

$$\begin{aligned} I &= \int_{z_0}^z \left(\frac{\mathcal{D}}{z} + \frac{\bar{\mathcal{D}}}{\bar{\zeta}} \right) \exp \left(-\frac{z\zeta}{4D_{\text{eff}}t} \right) d\zeta \\ &= \frac{4D_{\text{eff}}t}{z^2} \left[\exp \left(-\frac{zz_0}{4D_{\text{eff}}t} \right) - \exp \left(-\frac{z\bar{z}}{4D_{\text{eff}}t} \right) \right] \\ &\quad + \bar{\mathcal{D}} \log \left(\frac{\bar{z}}{z_0} \right) + \int_{z_0}^z \left[\exp \left(-\frac{z\zeta}{4D_{\text{eff}}t} \right) - 1 \right] \frac{\bar{\mathcal{D}}}{\bar{\zeta}} d\zeta \end{aligned} \quad (66)$$

is needed where the function $f(z, t)$ has been replaced by the real constant z_0 . It will be seen that $z_0 = 0$ in order for the transient solution to agree with the classical elasticity solution at $t = 0^+$, (64), and $t \rightarrow \infty$, (63). In that case (66) indicates that I diverges at the origin and generates a jump in $u_1 + iu_2$ and $F_1 + iF_2$ as in the classical elasticity. Notice also that this jump in I is independent of time. Thus, as Rice and Cleary (1976) observe, only the contribution of the integral which generates a function

with a branch cut associated with a jump in the displacement and force will be considered. Hence

$$I = \frac{4\mathcal{D}D_{\text{eff}}t}{z^2} \left[1 - \exp\left(\frac{z\bar{z}}{4D_{\text{eff}}t}\right) \right] + \mathcal{D} \log \bar{z} + \int_0^z \left[\exp\left(-\frac{z\zeta}{4D_{\text{eff}}t}\right) - 1 \right] \frac{\mathcal{D}}{\zeta} d\zeta. \quad (67)$$

Next, it is proposed that

$$\varphi(z, t) = A(t) \log z \quad \text{and} \quad \psi(z, t) = B(t) \log z, \quad (68)$$

so that the jump conditions generated by (67) and (68), when using them in (52) and (56), take the forms

$$2G\bar{b} = (3 - 4\nu)(-2\pi i)\bar{A}(t) - 2\pi i B(t) - 2\pi i \frac{\nu - \nu^\mu}{(1 - \nu)(1 - \nu^\mu)} \mathcal{D}, \quad (69)$$

$$i\bar{P} = -2\pi i \bar{A}(t) + 2\pi i B(t) + 2\pi i \frac{\nu - \nu^\mu}{(1 - \nu)(1 - \nu^\mu)} \mathcal{D}. \quad (70)$$

The solution to the system of equations (69) and (70) is time independent, i.e.

$$A(t) = A = \frac{\mathcal{D}}{1 - \nu} \quad \text{and} \quad B(t) = B = \frac{-2G\bar{b} + (3 - 4\nu^\mu)i\bar{P}}{8\pi i(1 - \nu^\mu)}. \quad (71)$$

Substituting this result into (68) and using (53) and (54) with $f(z, t) = 0$, one finds

$$\Phi(z, t) = \frac{1}{1 - \nu} \frac{\mathcal{D}}{z}, \quad (72)$$

in agreement with (62) at time $t = 0$ and $t \rightarrow \infty$, and

$$\Psi(z, t) = \frac{-2G\bar{b} + (3 - 4\nu^\mu)i\bar{P}}{8\pi i(1 - \nu^\mu)} \frac{1}{z}. \quad (73)$$

So the complex potentials $\Phi(z, t)$ and $\Psi(z, t)$ for the transient stress field are correspondingly the complex potential $\Phi(z)$ at time $t = 0^+$, i.e. at fixed solute composition, and the complex potential $\Psi(z)$ at time $t \rightarrow \infty$, i.e. at fixed solute chemical potential. The time-dependent stress field may now be obtained from (45) and (47). For this purpose the integral $\int_{z_0}^z \partial[C(z, \zeta, t) - C_0]/\partial z d\zeta$ is needed, and in fact with use of (65)

$$\begin{aligned} \int_{z_0}^z \frac{\partial[C(z, \zeta, t) - C_0]}{\partial z} d\zeta &= \frac{6(\nu - \nu^\mu)}{E(1 - \nu^\mu)} \frac{1}{\lambda\Omega} \left\{ \frac{8\mathcal{D}D_{\text{eff}}t}{z^3} \left[\exp\left(-\frac{z\bar{z}}{4D_{\text{eff}}t}\right) - \exp\left(-\frac{zz_0}{4D_{\text{eff}}t}\right) \right] \right. \\ &\quad + \frac{\mathcal{D}}{z^2} \left[z \exp\left(-\frac{z\bar{z}}{4D_{\text{eff}}t}\right) - z_0 \exp\left(-\frac{zz_0}{4D_{\text{eff}}t}\right) \right] \\ &\quad \left. + \frac{\mathcal{D}}{z} \left[\exp\left(-\frac{z\bar{z}}{4D_{\text{eff}}t}\right) - \exp\left(-\frac{zz_0}{4D_{\text{eff}}t}\right) \right] \right\}. \quad (74) \end{aligned}$$

By imposing the known elasticity solution at $t = 0^+$ and $t \rightarrow \infty$ in (47), one deduces $z_0 = 0$, as has already been mentioned, and hence

$$\int_{z_0}^z \frac{\partial[C(z, \zeta, t) - C_0]}{\partial \zeta} d\zeta = \frac{6(\nu - \nu^\mu)}{E(1 - \nu^\mu)} \frac{1}{\lambda \Omega} \left\{ \frac{8\mathcal{D}D_{\text{eff}}t}{z^3} \left[\exp\left(-\frac{z\bar{z}}{4D_{\text{eff}}t}\right) - 1 \right] \right. \\ \left. + \frac{\mathcal{D}}{z^2} z \exp\left(-\frac{z\bar{z}}{4D_{\text{eff}}t}\right) + \frac{\bar{\mathcal{D}}}{z} \left[\exp\left(-\frac{z\bar{z}}{4D_{\text{eff}}t}\right) - 1 \right] \right\}. \quad (75)$$

4.3.1. Application: an isolated edge dislocation. In the case of an isolated edge dislocation with Burgers vector \mathbf{b} parallel to the x_1 axis, as is shown in Fig. 2, $P = 0$ and $\mathcal{D} = Gb/4\pi i$. Then the solution for the concentration field to the linear transient hydrogen diffusion is given by (65) as

$$\frac{C}{C_0} = 1 - \frac{3}{2\pi} \frac{(\nu - \nu^\mu)}{(1 + \nu)(1 - \nu^\mu)} \frac{b}{c_0 \lambda} \frac{\sin \theta}{r} \exp\left(-\frac{r^2}{4D_{\text{eff}}t}\right), \quad (76)$$

and at $t \rightarrow \infty$, i.e. at equilibrium,

$$\frac{C}{C_0} = 1 - \frac{3}{2\pi} \frac{(\nu - \nu^\mu)}{(1 + \nu)(1 - \nu^\mu)} \frac{b}{c_0 \lambda} \frac{\sin \theta}{r}. \quad (77)$$

One may check the result of (77) by calculating the equilibrium hydrogen concentration directly from the nonlinear form (6) for the chemical potential of hydrogen. Using (16) and observing that at regions far away from the dislocation core the unstressed lattice, $\boldsymbol{\sigma} = \mathbf{0}$, is characterized by hydrogen concentrations at the nominal level C_0 , one finds that the condition $\nabla\mu = 0$ for neutral chemical potential yields

$$\frac{C}{C_0} = \exp\left(\frac{\lambda \Omega \sigma_{kk}}{3kT}\right) \quad (78)$$

as $t \rightarrow \infty$. Substituting into (78) the value for σ_{kk} as calculated from the classical

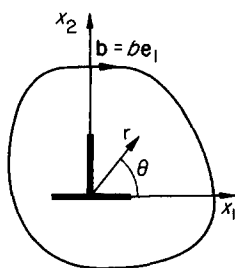


Fig. 2. An edge dislocation at the origin of the coordinates in the plane. Parameter b is the magnitude of the Burgers vector of the dislocation.

elasticity solution for the dislocation stress field with use of the moduli at fixed solute chemical potential yields the solution for the equilibrium concentration to the nonlinear transient hydrogen diffusion as

$$\frac{C}{C_0} = \exp \left(- \frac{3}{2\pi} \frac{(v - v^\mu)}{(1 + v)(1 - v^\mu)} \frac{b}{c_0 \lambda} \frac{\sin \theta}{r} \right). \quad (79)$$

Equation (79) which is a Boltzmann type of approximation (Hirth and Carnahan, 1978) predicts infinite solute concentration in the tensile side of the dislocation core and zero in the compressive. Comparing (77) and (79), one verifies that when the distance r from the dislocation core is large the solution (77) for the hydrogen concentration at equilibrium with local stress is equal to the first two terms in the Taylor series expansion of the concentration as is given by (79). This result indicates that the solution to linear diffusion is fairly accurate at regions remote from the core where the hydrogen concentration does not deviate markedly from the nominal value. Consequently the linear solution (77) is not expected to represent the hydrogen concentration field close to the core because the linearity condition of small $C - C_0$ is not met. In fact, as has already been discussed, (77) predicts for $0 < \theta < \pi$ negative hydrogen concentrations within a circular region whose cutoff radius increases with time. At equilibrium this radius is maximum and given by

$$\frac{r_0}{b} = \frac{3(v - v^\mu) \sin \theta}{2\pi c_0 \lambda (1 + v)(1 - v^\mu)}. \quad (80)$$

The cutoff radius r_0 at $\theta = \pi/2$ defines a circular region in which the linear solution (76) fails to be valid at least in the compressive side of the dislocation. It should be mentioned though that neither is the nonlinear solution (79) valid close to the core, where a Fermi–Dirac form (Hirth and Carnahan, 1978) is more appropriate than the Boltzmann approximation of (79). In Fig. 3, the equilibrium hydrogen concentration C/C_0 , as given by (77) and (79) in the H/Ta system, is plotted against the normalized distance r/b at $\theta = 3\pi/2$, (see Fig. 2), temperature 300 K and nominal hydrogen concentration of 0.1 H/Ta. Concentrations predicted by (77) are in agreement with those of the nonlinear solution (79) only when $r/b > 6$. The same result is also valid in the case of Nb/H and V/H systems. The linear solution fails to predict the hydrogen concentration very close to the dislocation core because of the prevailing severe concentration gradients which cannot be characterized by the linear hydrogen diffusion equation (22). Therefore the proposed linear solution (77) is only a far field solution.

The transient stress field is determined by observing that when $P = 0$ and $\mathcal{D} = Gb/4\pi i$ the complex potentials of (72) and (73) take the form

$$\Phi(z, t) = \frac{1}{1 - v} \frac{\mathcal{D}}{z} \quad \text{and} \quad \Psi(z, t) = - \frac{1}{1 - v^\mu} \frac{\mathcal{D}}{z}. \quad (81)$$

Substituting (65), (75) and (81) into (45) and (47) and using

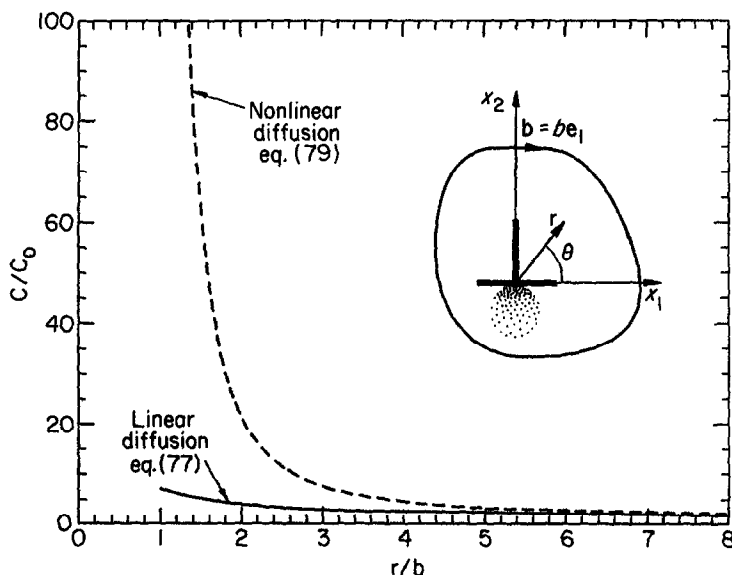


Fig. 3. Plot of the equilibrium hydrogen concentration C/C_0 at an edge dislocation with Burgers vector magnitude b in the H/Ta system versus normalized distance r/b at $\theta = 3\pi/2$, temperature 300 K, and nominal hydrogen concentration of 0.1 H/Ta.

$$\frac{\sigma_{rr} + \sigma_{\theta\theta}}{2} = \sigma \quad \text{and} \quad \frac{\sigma_{\theta\theta} - \sigma_{rr}}{2} + i\sigma_{r\theta} = \tau \exp(2i\theta), \quad (82)$$

one finds

$$\sigma_{rr} = \frac{\mu b}{2\pi(1-\nu)(1-\nu^\mu)} \left\{ -(1-\nu^\mu) - (v-\nu^\mu) \frac{4D_{\text{eff}}t}{r^2} \left[\exp\left(-\frac{r^2}{4D_{\text{eff}}t}\right) - 1 \right] \right\} \frac{\sin \theta}{r}, \quad (83)$$

$$\sigma_{\theta\theta} = \frac{\mu b}{2\pi(1-\nu)(1-\nu^\mu)} \left\{ -(1-\nu^\mu) + (v-\nu^\mu) \left[\frac{2 \exp\left(-\frac{r^2}{4D_{\text{eff}}t}\right) + \frac{4D_{\text{eff}}t}{r^2} \left(\exp\left(-\frac{r^2}{4D_{\text{eff}}t}\right) - 1 \right)}{r^2} \right] \right\} \frac{\sin \theta}{r}, \quad (84)$$

$$\sigma_{r\theta} = \frac{\mu b}{2\pi(1-\nu)(1-\nu^\mu)} \left\{ (1-\nu^\mu) + (v-\nu^\mu) \frac{4D_{\text{eff}}t}{r^2} \left[\exp\left(-\frac{r^2}{4D_{\text{eff}}t}\right) - 1 \right] \right\} \frac{\cos \theta}{r}. \quad (85)$$

The time necessary for equilibrium to be reached depends on the material parameters, temperature, and nominal concentration C_0 of the system. Figure 4 shows the evolution in time of the hydrostatic stress σ_{kk} at several positions r/b in the tension side of an edge dislocation along the radius at $\theta = 3\pi/2$ in Ta when the system temperature is 300 K and its nominal concentration is 0.1 H/Ta. Stress σ_{kk} evolves from σ_{kk}^0 at

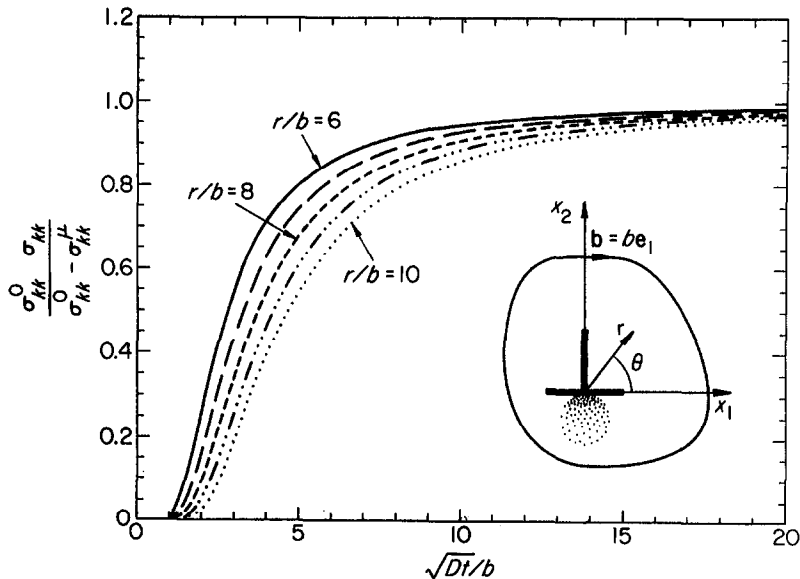


Fig. 4. Plot of the hydrostatic stress σ_{kk} at $\theta = 3\pi/2$ for fixed normalized position r/b against normalized time \sqrt{Dt}/b in Ta at 300 K and nominal concentration of 0.1 H/Ta. Stress σ_{kk} equals to σ_{kk}^0 at fixed solute concentration 0.1 H/Ta at time $t = 0$ and to σ_{kk}^μ at fixed solute chemical potential when relaxation has been reached.

fixed solute concentration C_0 at time $t = 0$ toward σ_{kk}^μ at fixed solute chemical potential. After time $\sqrt{Dt}/b = 1$ the stress begins clearly to deviate from σ_{kk}^0 and by the time $\sqrt{Dt}/b = 20$ the stress σ_{kk}^μ at relaxation has almost been reached. Given that $D = 1.97 \times 10^{-10}$ m²/s for Ta nondimensionalized time 20 corresponds to 1.66×10^{-5} s of real time. Therefore, relaxation of the hydrogen concentration and stress around dislocation cores to the corresponding equilibrium values can be achieved almost instantaneously. In Fig. 5 the shear stress σ_{12}^μ due to dislocation at fixed solute chemical potential normalized by the shear stress σ_{12}^0 at fixed solute composition is plotted against the nominal hydrogen concentration c_0 . The shear stress ratio $\sigma_{12}^\mu/\sigma_{12}^0 = (1 - \nu)/(1 - \nu^\mu)$ is less than unity and decreases as the nominal concentration becomes larger. This is in agreement with concentration dependence of the Poisson's ratio ν^μ at fixed solute chemical potential which is less than the Poisson's ratio ν at fixed solute composition, as is shown in Fig. 1.

5. IMPLICATIONS FOR DISLOCATION PLASTICITY AND FRACTURE

Using the constitutive description of the hydrogen-metal binary system in conjunction with standard linear elasticity results for lattice defect interactions, one may draw some important conclusions about the hydrogen effect on the deformation of materials under fixed solute chemical potential conditions of hydrogen diffusion (Rice, 1992a).

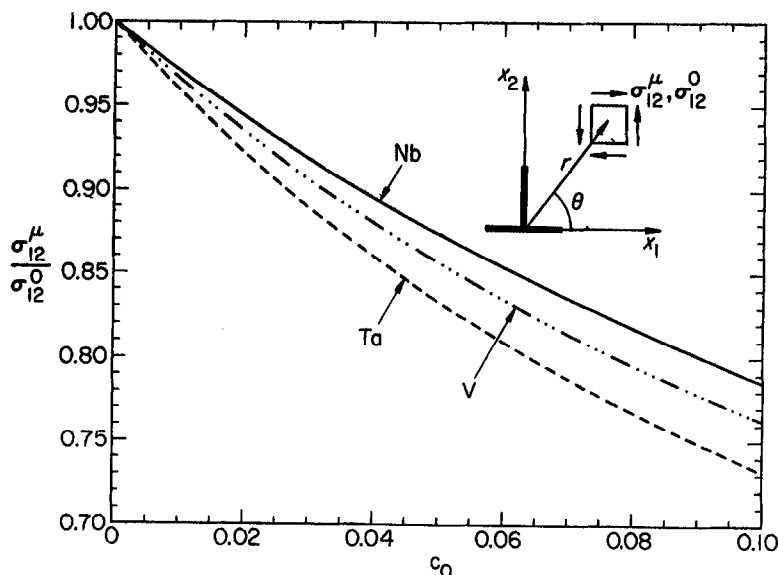


Fig. 5. Plot of the shear stress σ_{12}^μ due to dislocation at fixed solute chemical potential normalized by the shear stress σ_{12}^0 at fixed solute composition against nominal hydrogen concentration c_0 in the Ta/H, Nb/H and V/H systems at temperature 300 K.

The interaction force between two parallel edge dislocations (Hirth and Lothe, 1982) is proportional to $G/(1-\nu^e)$, where $\nu^e = \nu$ at fixed solute composition and $\nu^e = \nu^\mu$ at fixed solute chemical potential. Thus the ratio of the interaction force at fixed solute chemical potential to the interaction force at fixed solute composition is equal to the ratio $\sigma_{12}^\mu/\sigma_{12}^0$ which is plotted versus nominal concentration in Fig. 5. Therefore the interaction between two edge dislocations becomes smaller when the hydrogen in solution reaches equilibrium with the local stress. In addition the reduction in the interaction force at equilibrium increases with increasing nominal concentration, a result which has also been found by Sofronis and Birnbaum (1995). It should be mentioned that weakening of the interaction between edge dislocations is the physical basis of the hydrogen-enhanced localized plasticity (HELP) model of hydrogen embrittlement (Sirois *et al.*, 1992; Birnbaum and Sofronis, 1994).

The energy per unit length of an edge dislocation is proportional to $G/(1-\nu^e)$ and that of a screw dislocation is proportional to G . It is very likely that the Poisson's ratio ν^μ at fixed solute chemical potential may become negative, locally, close to the dislocation core where large hydrogen accumulation is predicted. As a consequence, segments of edge dislocations become energetically more favorable than those of screw dislocations since the energy of an edge dislocation is less than the energy of a screw dislocation. Therefore hydrogen may limit the ability of dislocations to cross slip. Ulmer and Altstetter (1991) suggested this effect as a possible mechanism of hydrogen-induced cracking by proposing that hydrogen provides a force which tends to maintain the dislocations in the edge configuration, making relaxation of the pile up stress field by screw dislocation cross slip more difficult.

The Griffith theory of brittle fracture and the new theory of Rice (1992b) for

dislocation nucleation from a crack tip suggest that the critical stress intensity factor, squared, is proportional to $G/(1-\nu^e)$ multiplied either by the surface energy, $2\gamma_s$, or by the unstable stacking energy γ_u . Therefore, at equilibrium conditions, hydrogen provides an additional and unexpected effect by reducing the multiplying factor $G/(1-\nu^e)$ which may assist in triggering dislocation injection at a crack tip or crack propagation. This extra effect may act synergistically with the decrease on the surface energy caused by absorbed hydrogen on a clean surface or with a probable reduction of the unstable stacking energy. The reduction of the surface energy is pertinent to the decohesion mechanism of hydrogen embrittlement but the main difficulty in this theory lies in relating the surface energy or other physical parameters (Birnbaum, 1979) to the fracture stress and the local hydrogen concentration. A thorough assessment of the present unexpected effect on dislocation plasticity and fracture should await experimental measurements of microscopic parameters such as stacking fault energy or surface energy (Robertson and Birnbaum, 1995) in the presence of hydrogen.

6. CLOSURE

An analysis has been presented which describes the coupling of lattice linear hydrogen diffusion with the linear elastic deformation of a solid-containing mobile interstitial hydrogen in solid solution.

The linear hydrogen diffusion is governed by the standard Fick's law in which the normal lattice diffusion constant has been replaced by an effective diffusion constant in order to account for the drift due to hydrostatic stress. The effective diffusion constant depends only on the nominal hydrogen concentration, the system's temperature, the hydrogen and solvent material parameters, and does not depend on stress. Therefore the existing diffusion solutions for various specimen geometries can be used to study hydrogen diffusion under stress at given nominal solute concentration. As an example, the coupled transient field equations were solved analytically in the case of hydrogen diffusing toward the tension side of the core of an isolated edge dislocation in an infinite medium under plane strain deformation conditions.

The constitutive response of the solid solution at fixed solute chemical potential was found to resemble that of a fluid-infiltrated porous material during drained deformation at constant pore pressure or the thermoelastic response of a solid under adiabatic straining. The linear elastic moduli at fixed solute chemical potential have been calculated as functions of the nominal hydrogen concentration in terms of the moduli at fixed solute nominal composition and the material parameters and temperature of the system. Therefore when the hydrogen distribution relaxes to the equilibrium values dictated by the local stress, the hydrogen effect on the linear elastic constitutive behavior is depicted in and modeled through the constitutive moduli. The implications of this result are important in understanding the hydrogen effect on dislocation plasticity and fracture of metals and alloys. Thus, using the linear elastic results for the dislocation stress fields, one deduces that hydrogen causes material softening by reducing the interaction between edge dislocations, enhances the planarity of slip by reducing the strain energy of an edge dislocation relative to the strain

energy of a screw dislocation, decreases the intensity of the loads required to cause a crack to propagate, and assists the dislocation injection ahead of a crack tip according to Rice's (1992b) new theory for dislocation nucleation. These effects are in excellent agreement with the hydrogen enhanced localized plasticity model of hydrogen embrittlement proposed by Sirois and Birnbaum (1992) and Birnbaum and Sofronis (1994).

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