STRAIN INDUCED DIFFUSION OF HYDROGEN IN Pd ALLOY MEMBRANES

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ABSTRACT: An equation for the diffusion flux of hydrogen through thin slab shaped membranes is derived. The effect of an induced elastic field on the diffusion flux is demonstrated. A comparison of the published experimental result with the outlined theory is given.

Introduction

The behaviour of hydrogen in a metal lattice has been a stimulating study for many research workers. Very recently abnormal behaviour of hydrogen diffusion in Pd alloy membranes was reported and interpreted as uphill diffusion of hydrogen by Lewis and his co-workers (Lewis *et al.* 1983; Lewis *et al.*1987). This conclusion was based on the observed diffusion of hydrogen in Pd alloy membranes towards high concentration regions from low concentration regions. The inclusion of hydrogen in a metal lattice is usually associated with lattice expansion (Kandasamy 1980 and Peisl 1978) which creates an elastic field in the lattice. The effect of lattice deformation, due to application of an external stress on diffusion of interstitial solutes, such as hydrogen, has been a long standing study for many scientists. Their studies have shown that the interstitial solutes preferentially diffuse from regions of relatively compressed interstitial sites to regions of relatively expanded sites (Wagner 1978; Kehr 1978). In this paper an expression for internally induced elastic stress on the inclusion of hydrogen during the diffusion process in a thin slab lattice is derived and its effect on the diffusion of hydrogen is discussed and compared with published results (Lewis *et al.* 1987).

Theory

a) Derivation of an equation for elastic stress induced by the diffusing interstitials in thin slab lattice.

Consider a thin slab geometry with the space co-ordinates illustrated in figure 1. Assume homogeneous distribution of interstitials as a strees free reference state. A change in the distribution of interstitial concentration from homogeneity will result in the introduction of internal stresses. Assume a change $\triangle c$ in the concentration of interstitial distribution from its homogeneous value due to the absorption of hydrogen through the YZ face at

$X = O$. In general Δc is a function of space and time t, since the absorption is controlled by the diffusion. The part of the lattice which absorbs interstitials is expanded. The internal stress that is responsible for the expansion comes from interstitials and it can be expressed as $\sigma_c = K\Delta c$ where K is a positive constant (Cermak and Kufudakis 1976). This expansion caused by the composition change will be opposed by the remaining part of the lattice by elastically developing an internal stress, σ_e.

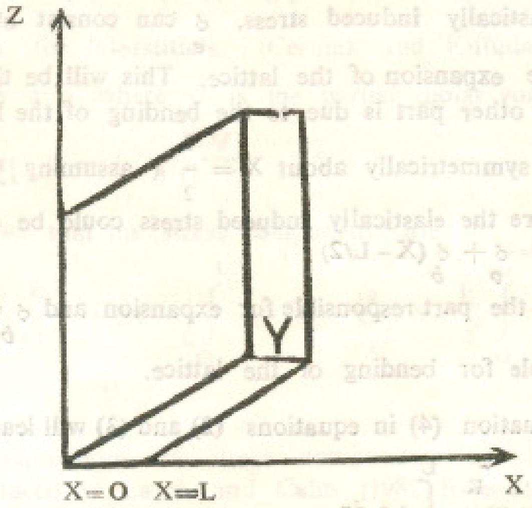

Fig. 1. Thin slab geometry with space coordinates (XYZ). The thickness L of the slab is very small compared to the width and the length.

Therefore the total internal stress σ_i is given by

$$\sigma_i = \sigma_c + \sigma_e = K\,\Delta c + \sigma_e \qquad (1)$$

Assume the diffusion is only along the X direction. This is similar to assuming a constant concentration of interstitials in the YZ plane. Then in the slab material the component of the internal stress along the Y direction, σ_{YY} is the same as the stress component along the Z direction, σ_{ZZ} and the stress component along the X direction σ_{XX} is zero (Timoshenko 1934). The slab is under static equilibrium. Therefore the net force on the slab and the momentum about $X = L/2$ should be zero.

From zero net force $K \int_O^L \Delta c \, dx + \int_O^L \sigma_e \, dx = 0$ (2)

From zero momentum about $X = \frac{1}{2} L$

$$K \int_O^L \Delta c \left[x - \frac{L}{2}\right] dx + \int_O^L \sigma_e \left[x - \frac{L}{2}\right] dx = 0 \qquad (3)$$

In general the elastically induced stress, σ_e can consist of two parts. One part is due to the expansion of the lattice. This will be the same everywhere in the slab. The other part is due to the bending of the lattice. This should vary linearly and symmetrically about $X = \frac{L}{2}$ (assuming constant Young's modulus). Therefore the elastically induced stress could be expressed as

$$\sigma_e = \sigma_o + \sigma_b (X - L/2) \qquad (4)$$

where σ_o represents the part responsible for expansion and $\sigma_b (X - L/2)$ represents the part responsible for bending of the lattice.

Substitution of equation (4) in equations (2) and (3) will lead to the following:

$$\sigma_o = -\frac{K}{L} \int_O^L \Delta c \, dx \qquad (2a)$$

$$\sigma_b = -12 \frac{K}{L^3} \int_O^L \Delta c \left[x - \frac{L}{2}\right] dx \qquad (3a)$$

Therefore the internal stress componets σ_{YY}, σ_{ZZ} can be given by

$$\sigma_{YY} = \sigma_{ZZ} = K \left\{ \Delta c - \frac{1}{L} \int_O^L \Delta c \, dx - \frac{12}{L^3} \left[X - \frac{L}{2}\right] \int_O^L \Delta c \left[X - \frac{L}{2}\right] dx \right\}$$

The hydrostatic (external) stress components which have an equal effect on the lattice are equivalently given by

$$\sigma_{YY} = \sigma_{ZZ} = -K \left\{ \Delta c - \frac{1}{L} \int_O^L \Delta c \, dx - \frac{12}{L^3} \left[X - \frac{L}{2}\right] \int_O^L \Delta c \left[X - \frac{L}{2}\right] dx \right\} \qquad (5)$$

For the problem considered here, that is with equal tensile stresses in the Y and Z directions and zero stress in the X direction, the strain ε and stress σ can be related by

$$\sigma = \frac{E\varepsilon}{(1-\nu)}$$

where E is the Young's modulus and ν is the Poisson's ratio. If we assume Young's modulus and Poisson's ratio to be constant then

$$K = \frac{d\sigma}{dc} = \frac{E}{(1-\nu)} \quad \frac{d\varepsilon}{dc}$$

Using Vegard's law for interstitials, (Cermak and Kufudakis 1976), $\frac{d\varepsilon}{dc}$ can be replaced by $\frac{1}{3}\bar{V}$ where $\bar{V}$ is the partial molar volume of interstitials

$$\text{Therefore} \quad K = + \frac{E\bar{V}}{3(1-\nu)}$$

From this it follows that the stress components are

$$\sigma_{YY} = \sigma_{ZZ} = -\frac{E\bar{V}}{3(1-\nu)}\left\{\Delta c - \frac{1}{L}\int_{O}^{L}\Delta c\, dx - \frac{12}{L^3}\left[X - \frac{L}{2}\right]\int_{O}^{L}\Delta c\left[X - \frac{L}{2}\right]dx\right\}$$

and $\sigma_{XX} = 0.$ (6)

The above expressions for stress components are exactly identical to the expressions deduced by Larche and Cahn (1982) from the theory of thermoelasticity.

b) Derivation of equation for diffusion flux in the presence of induced internal stresses

In general the diffusion flux of hydrogen J_H could be written as (Volkl and Aleffeld 1978 and Wipf 1976)

$$J_H = - Mc \text{ grad } \mu \quad (7)$$

where M is mobility, c is concentration and μ is the chemical potential of hydrogen in the solid. The chemical potential of hydrogen in a solid which is under a tensile stress μ (c, σ) could be expressed as (Flanagan and Lynch 1976)

$$\mu(c, \sigma) = \mu(c, o) - \bar{V}_H \sigma \quad (8)$$

Where $\bar{V}$ is the partial molar volume of hydrogen in the solid and μ (c, o) is the chemical potential in stress free state. If μ^{O}_{H} is the standard chemical potential of hydrogen atom then

$$\mu(c,\sigma) = \overset{o}{\mu}_H + RT \ \ln c \qquad (9)$$

Where R and T have their usual meaning. Since the chemical potential of hydrogen is a function of c and σ equation (7) can be expanded as,

$$J_H = -Mc\,\{\text{grad}\ \mu\,(c,o) + \frac{d\mu}{d\sigma}(c,\sigma)\ \text{grad}\ \sigma\}$$

$$= -Mc\,\frac{d\mu}{dc}(c,o)\ \text{grad}\ c - Mc\,\frac{d\mu}{d\sigma}(c,\sigma)\ \text{grad}\ \sigma \qquad (10)$$

But from equation (8) $\frac{d\mu}{d\sigma}(c\,\sigma) = -\bar{V}_H$ and the quantity

$Mc\,\frac{d\mu}{dc}(c,o)$ could be defined as the diffusion coefficient, D_H

Equation (10) can then be written as

$$J_H = -D_H\ \text{grad}\ c + \frac{D_H\ \bar{V}_H}{\frac{d\mu}{dc}(c,o)}\ \text{grad}\ \sigma$$

But from equation (9) $\frac{d\mu\,(c,o)}{dc} = \frac{RT}{c}$

Therefore $J_H = -D_H\ \text{grad}\ c + \frac{c\ D_H\ \bar{V}_H}{RT}\ \text{grad}\ \sigma$

Chen Min Li (1978) has suggested a similar equation to explain the possibility of enhanced diffusivity of isotropic solute in solid lattice. In a previous paper the author (Kandasamy 1989) has used the Chen Min Li formalism to explain the experimental result of Lewis *et al.* (1987). Here the equation has been derived from basic principles. On substitution for grad σ from expression (6) for the stress components, the flux J_H is given by

$$J_H = -D_H\{1 + \frac{2\,\bar{V}_H\,c\,E}{3\,R\,T}\}\,\frac{dc}{dx} + \frac{8\,\bar{V}^2_H\ E\,c\,D_H}{L^3\,R\,T}\int_0^L \Delta c\,[x - L/2]\,dx \qquad (11)$$

Discussion

Equation (11) for the diffusion flux of hydrogen can be written as

$$J_H = - D^*_H \frac{dc}{dx} + \frac{8\,\bar{V}_H^2\, E\, c\, D_H}{L^3 R T} \int_0^L \Delta c\,[x - L/2]\,dx \qquad (12)$$

where $D^*_H = D_H \{ 1 + \frac{2\,\bar{V}_H\, c\, E}{3 R T} \}$

The first term of equation (12) is identical to Fiction flux term but with an enhanced diffusion coefficient due to elastically induced stress (extension part). The variation of this term with time could be represented by the characteristic break through nature (Crank 1972) as illustrated by plot (a) in figure (2). The second term also represents the effect of an elastically induced stress (bending part) due to the inhomogenity of hydrogen distribution during diffusion process. We can show that this effect generates a hydrogen flux in the negative X direction, that is a flux against the concentration gradient. To illustrate this consider the second term of equation (12) at short times, that is when $D_H t/L^2 << 1$ then the integral $\int_0^L \Delta c\,[x - L/2]\,dx$ can be approximated by $-\int_0^L \Delta c\,dx$ which is equal to $-\frac{L^2}{2}\Delta c_O\,(D_H t/L^2)^{1/2}$ where Δc_O is the concentration change at x=o. Therefore the second term of equation (12) is

$$\frac{-4\,\bar{V}_H^2\, c E D_H}{R T}\,\frac{\Delta c_O}{L}\,(D_H t/L^2)^{1/2},$$

which represents a flux in the negative direction. After a very long time, that is when $D_H t/L^2 > 0.45$ say, we could assume the establishment of a steady state of diffusion (Crank 1972). At steady state of diffusion we could assume linear variation of the concentration across the slab thickness. At this state the second term of equation (12) is $\frac{-2\,\bar{V}_H^2\, c E D_H}{3 R T}\,\frac{\Delta c_O}{L}$ This also represents flux in the negative X direction. Therefore the variation of the second term of equation (12) could be represented by plot (c) in figure (2). This is in qualitative agreement with the published results of Lewis *et al.* (1987) which are reproduced in plot (d) of figure (2).

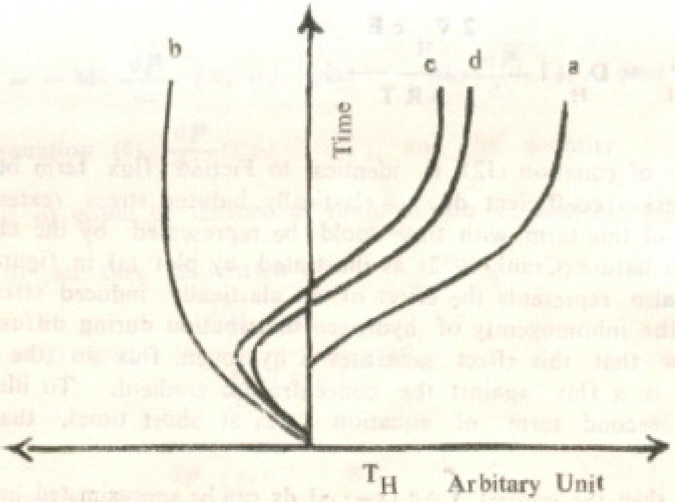

Fig. 2. Plot *(a)* Variation with time (t) of the first term of equation (12) for hydrogen flux J_H

Plot *(b)* Variation with time (t) of the second term of equation (12) for hydrogen flux J_H

Plot *(c)* Variation with time (t) of the diffusion flux J_H given by equation (12)

Plot (d) Experimental diffusion flux J_H with time (Lewis *et al.* 1987).

Conclusion

An expression for the stress induced by compositional inhomogeneity can be derived from simple Vegard's law. The observed abnormal behaviour of hydrogen diffusion can be accounted for by including the effect of stress induced by the compositional changes in the diffusion process.

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