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Effect of diffusion coefficient variation on interrelation between hydrogen diffusion and induced internal stress in hydrogen storage alloys



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ABSTRACT

A diffusion behavior of hydrogen in a hydrogen storage alloy is affected by not only hydrogen concentration but also the stress induced by hydrogen atom expanding the lattice of the alloy. The uphill diffusion in which hydrogen diffused against the concentration gradient due to the stress has been observed. Moreover, the fugacity of hydrogen in the alloy deviates from unity significantly even at low hydrogen concentration, which decreases the flux.

In this paper, the effect of the stress and the diffusion coefficient variation with the concentration on hydrogen diffusion at low concentration was investigated using the finite element analysis. As a result, the variable diffusion coefficient model combined with the stress effect showed better agreement with the experimental result than Fick's diffusion models and the constant coefficient SID model. It was concluded that the effect should be considered even if the concentration is low.

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1. Introduction

Hydrogen-storage-alloy actuators have been developed by many researchers, which operate by the volume increase of the alloy in hydrogen absorption [1-3]. Its static performance can be determined from the hydrogen solubility of the alloy and the mechanical properties of the materials constituting the actuator. Its kinetic behavior depends on the diffusion of hydrogen in the alloy, therefore, the knowledge of hydrogen diffusion is important to investigate the kinetic behavior of the hydrogen-storage-alloy actuators.

The diffusion flux is induced by the chemical potential gradient. The stress effect on the flux should be considered in hydrogen storage alloys because they are subjected to the large internal stress induced by the lattice expansion when hydrogen atom intrudes in the alloys. Considering stress in solids, Fick's law under which the flux is proportional to the concentration gradient, is revised as Eq. (1) on the basis of the thermodynamics (Appendix A).

$$J = -D\nabla C + \frac{DCV_H}{RT}\nabla\sigma_h \tag{1}$$

where *J* is the hydrogen flux, *D* is the diffusion coefficient of hydrogen in the alloy, *C* is the hydrogen concentration, *V*_H is the partial molar volume of hydrogen in the alloy, *R* is the gas constant, *T* is temperature and σ_h is the hydrostatic stress represented as $\sigma_h = 1/3(\sigma_r + \sigma_\theta + \sigma_z)$.

The stress induced diffusion (SID) of hydrogen in metals has been investigated experimentally and numerically in many papers [4–17]. Wriedt and Oriani [4] and Bockris et al. [5] showed the decrease in hydrogen solubility and permeability by the stress when loads were applied to $Pd_{75}Ag_{25}$ alloy and a steel, respectively. Lewis et al. [6–8], Baranowski [9] and Kandasamy et al. [10,11] showed the flux arising contrary to the hydrogen concentration gradient in tubular membranes of $Pd_{81}Pt_{19}$, which was caused by the stress gradient induced by the lattice expansion of the alloy. The effect of the stress induced by the lattice expansion on diffusion was investigated with numerical analyses [12–17].

In hydrogen storage alloys, the diffusion coefficient of hydrogen cannot be regarded as a constant even at low hydrogen concentration, though it was assumed to be constant in the previous paper



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Nomenclature		V_H	partial molar volume of hydrogen in metal
		w	weighting function
С	hydrogen concentration in metal $(=C_0 n_H)$	[N]	shape function
C_0	hydrogen concentration in metal corresponding to	[B]	differential form of shape function $(= \nabla \cdot [N])$
	$n_H = 1$	[M]	mass matrix
D	apparent diffusion coefficient of hydrogen	$[K_1]$	stiffness matrix
D_0	diffusion coefficient of hydrogen at $n_H = 0$	$[K_2]$	stiffness matrix of stress effect term
Ε	Young's modulus	$\{F\}$	force vector
е	$1/3(\varepsilon_r + \varepsilon_{ heta} + \varepsilon_z)$		
F	factor showing ratio of hydrogen flux to Fick's diffusion	Greek symbols	
	flux at same concentration gradient	α	constant
f	fugacity	β	linear expansion ratio induced by hydrogen insertion
f_{x}	concentration correction term of diffusion coefficient	ε	normal strain
J	hydrogen flux	ν	Poisson's ratio
k	constant	μ	chemical potential
п	normal vector	μ_H^0	chemical potential in standard state
n_H	molar ratio of hydrogen in metal	γ	shear strain
п _{Н,0}	molar ratio of hydrogen in metal corresponding to	σ	stress
	$\sigma_h=0$	σ_h	hydrostatic stress (=1/3($\sigma_r + \sigma_\theta + \sigma_z$))
Р	pressure		
P_0	pressure at initial condition	Subscripts and superscripts	
R	universal gas constant	Fick	Fick's diffusion
r	radius	Н	hydrogen atom
S	surface area	H_2	hydrogen gas
Т	temperature	in	at inner surface
t	time	out	at outer surface
и	displacement	r, θ, z	cylindrical coordinate axes
u_{σ}	self-stress factor [13]	S	surface
V	volume	t	tube

[12–17]. This is because its fugacity deviates from unity significantly. Dudek [18] investigated the variation of the diffusion coefficient in $Pd_{89}Pt_{19}$ alloy with hydrogen pressure using a tubular membrane, which revealed the diffusion coefficient of $8.0 \times 10^{-12} \text{ m}^2/\text{s}$ at hydrogen pressure of 30.19 kPa (corresponding to the atomic ratio of hydrogen to metal of 1.13 mol%) decreased to $6.3 \times 10^{-12} \text{ m}^2/\text{s}$ at 70.45 kPa (2.05 mol%). Thus, using the constant diffusion coefficient might cause a large error in the kinetic performance obtained from the diffusion analyses at the condition that the alloy absorbs a large amount of hydrogen, e.g. for the hydrogen storage-alloy actuator.

The aim of this paper is to demonstrate the necessity of the variable diffusion coefficient for the hydrogen diffusion analyses of hydrogen storage alloys. For this purpose, the effect of the SID and the diffusion coefficient variation with the concentration on hydrogen diffusion at low concentration was evaluated using the finite element analysis. Coupling analysis of diffusion and stress was attempted to consider the lattice expansion induced by hydrogen (Fig. 1).

2. Analysis method

In this paper, the diffusion coefficient of hydrogen in the hydrogen storage alloy was changed depending on the hydrogen concentration based on the analytical condition used in Ref. [18]. The dependence of the diffusion coefficient on the hydrogen concentration, n_H , was obtained by approximating the experimental values in Refs. [9,18] by a quadratic polynomial (Eq. (2)).

$$D = D_0 \cdot f_x = D_0 \left(1 - 23.1n_H + 186n_H^2 \right)$$
(2)

Eq. (2) showed good agreement with [19].

An analytical model was an axisymmetric 2D model of the $Pd_{81}Pt_{19}$ tube with the inner diameter of 4.00 mm, the thickness of 0.50 mm and the length of 0.075 mm as shown in Fig. 2. The material parameters were shown in Table 1 [9,14,20]. The symmetric condition was applied on the both ends of the model so as to assume an infinite length tube. The model was discretized with a four-node quadrilateral element 0.0125 mm on a side. The evaluation was performed at each integration point using the commercial FEM software package ANSYS 15.0.

The hydrogen diffusion was simulated by one-way coupling of the diffusion and structural analyses based on the technique used in the hydrogen embrittlement evaluation [21-25]. Eq. (1) was transformed into the finite element equation according to [21] (Appendix A) and implemented in ANSYS 15.0. The flow chart of the analyses is shown in Fig. 1. In the diffusion analysis, the boundary conditions of the concentration were applied on the inner and outer surfaces. It was assumed that the dissolved hydrogen at the both surfaces was held in equilibrium with the surrounding hydrogen gas. The concentration was calculated from Eq. (3).

$$n_H = n_{H,0} \exp\left(-\frac{V_H \sigma_h}{RT}\right) \tag{3}$$

where $n_{H,0}$ represents the concentration under free stress, which was calculated from the inner and outer pressures, P_{in} and P_{out} , with a quadratic approximation curve based on [18] (Eq. (4)).

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