EFFECT OF TRAPPING ON HYDROGEN
PERMEATION IN COPPER

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ABSTRACT - Permeation experiments with high-purity copper in a deuterium atmosphere suggest that reversible trapping of deuterium occurs. Deuterium permeation was measured at temperatures between 270 and 450°C. A mathematical model, based on the general diffusion-plus-trapping model of McNabb and Foster, was developed to predict trap densities. Solutions were obtained for a plane sheet by the finite-difference method and are convergent and stable over a relatively wide range of parameters. Experimental results agree qualitatively with predictions of the model.

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INTRODUCTION

Hydrogen permeation through metallic foils is commonly analyzed on the basis that simple interstitial diffusion is the rate controlling process.¹ Significant changes in the permeation behavior from surface effects, internal chemical reactions, and trapping have been observed in some metals and alloys.²⁻⁴ If any of these effects are present, models are available which predict how the permeation process is altered and provide a means for analyzing the experimental data. Several models for diffusion with concurrent trapping have been proposed, some of which were derived to treat specific problems.^{1,5-7} A general trapping model adaptable to many boundary and initial conditions has been formulated by McNabb and Foster.^{8,9} This paper shows that an approximate solution to their equations for the case of permeation may be obtained by the finite-difference method. A mathematical model is described based on experimental data for deuterium permeation through copper foils.

DEVELOPING THE MATHEMATICAL MODEL

The McNabb and Foster mathematical analysis of trapping describes diffusion with the relations

$$\frac{\partial u}{\partial \tau} + \frac{\partial w}{\partial \tau} = \nabla^2 u \quad (1)$$

$$\frac{\partial w}{\partial \tau} = \lambda u - \mu w - \nu u w \quad (2)$$

The variables in these equations are all dimensionless and are defined as follows for the case of one dimensional permeation:

$u = C/C_0$ where C is the concentration of diffusant, particles/cc at X , and C_0 is the concentration at the surface, $X = 0$

$w = n N/C_0$ where N is the number of traps/cc, and n is the fraction occupied

$\tau = Dt/a^2$ where D is the lattice diffusivity (cm^2/sec), t is the time (sec), and a is the specimen thickness (cm)

$X = x/a$ where a is the foil thickness, and x is distance (cm) from the foil surface

The parameters λ , μ , and ν describe the rates at which atoms are captured and released from the traps and are defined as follows:

$$\lambda = N\kappa a^2/D \quad (3)$$

$$\mu = \rho a^2/D \quad (4)$$

$$\nu = C_0 \kappa a^2/D \quad (5)$$

where κ and ρ are such that the number of atoms captured per second in a volume (δV) is $\kappa CN(1-n) \delta V$, and the number released per second in the volume (δV) is $\rho nN \delta V$. The value, ρ , is assumed to be dependent on temperature and the nature of the trap, but is independent of the local concentrations of diffusing and trapped hydrogen.

Inspection shows that the parameters λ , μ , and ν control the general nature of the diffusion equations. If all three parameters are zero, the equations reduce to those for simple diffusion with a constant D . If μ is zero, the equations describe irreversible trapping or chemical reaction. If ν is zero, reversible trapping is described by the equations, which now become linear. Each of these cases has been treated previously, and formal solutions are known.¹

The more general diffusion equation is non-linear and is not amenable to a formal solution; therefore, the finite difference method has been applied to obtain u and w as functions of time and position. The differential equations are solved with boundary conditions

$$u(0, \tau) = u_0^n = \text{constant} \quad (6)$$

$$u(1, \tau) = u_M^n = \text{constant} \quad (7)$$

where

$$u_1^0, u_2^0, \dots, u_{M-1}^0 \quad (8)$$

and

$$w_0^0, w_1^0, \dots, w_M^0 \text{ are initial values} \quad (9)$$

Subscripts and superscripts in the above equations give the space and time positions, respectively.

The following definitions were used to rewrite the differential equations as finite difference equations by neglecting higher order terms in the Taylor expansions

$$p_m = u_m^{n+1} - u_m^n \quad (10)$$

$$q_m = w_m^{n+1} - w_m^n \quad (11)$$

$$u_m^{n+1} = u_m^n + \partial u / \partial \tau \big|_m^n \Delta \tau + \dots \quad (12)$$

$$u_{m+1}^n = u_m^n + \partial u / \partial X \big|_m^n (\Delta X) + \frac{1}{2} \partial^2 u / \partial X^2 \big|_m^n (\Delta X)^2 + \dots \quad (13)$$

$$[uw]_m^{n+1} = [uw]_m^n + u \partial w / \partial \tau \big|_m^n \Delta \tau + w \partial u / \partial \tau \big|_m^n \Delta \tau + \dots \quad (14)$$

The diffusion equations then become

$$\frac{p_m}{\Delta \tau} + \frac{q_m}{\Delta \tau} = \frac{\theta (u_{m+1}^{n+1} - 2u_m^{n+1} + u_{m-1}^{n+1})}{(\Delta X)^2} + (1-\theta) \frac{(u_{m+1}^n - 2u_m^n + u_{m-1}^n)}{(\Delta X)^2} \quad (15)$$

and

$$q_m / \Delta\tau = \theta [\lambda u_m^{n+1} - \mu w_m^{n+1} - \nu u_m^{n+1} w_m^{n+1}] + (1-\theta) [\lambda u_m^n - \mu w_m^n - \nu u_m^n w_m^n] \quad (16)$$

where θ is a parameter that allows admixture both forward and backward in time. These equations yield the following relations after suitable expansion and rearrangement

$$-A_m p_{m+1} + B_m p_m - C_m p_{m-1} = D_m \quad (17)$$

$$q_m = R_m p_m + S_m \quad (18)$$

where

$$R_m = \frac{\theta [\lambda - \nu w_m^n]}{\theta [\mu + \nu u_m^n] + 1/\Delta\tau} \quad (19)$$

$$S_m = \frac{\lambda u_m^n - \mu w_m^n - \nu u_m^n w_m^n}{\theta [\mu + \nu u_m^n] + 1/\Delta\tau} \quad (20)$$

$$A_m = + \theta \quad (21)$$

$$B_m = \frac{(\Delta X)^2}{\Delta\tau} + \frac{(\Delta X)^2}{\Delta\tau} R_m + 2 \theta \quad (22)$$

$$C_m = + \theta \quad (23)$$

$$D_m = u_{m+1}^n - 2u_m^n + u_{m-1}^n - S_m \frac{(\Delta X)^2}{\Delta\tau} \quad (24)$$

The second relation gives q_m in terms of p_m so that the equations need only to be solved for p explicitly. If one boundary condition is known, $p_m = E_m p_{m+1} + F_m$. By substituting $(E_{m-1} p_m + F_{m-1})$ for p_{m-1} in the above, recursion relations for E_m and F_m are obtained:

$$E_m = \frac{A_m}{B_m - C_m E_{m-1}} \quad (25)$$

$$F_m = \frac{D_m + C_m F_{m-1}}{B_m - C_m E_{m-1}} \quad (26)$$

From the boundary conditions, $E_0 = F_0 = 0$, $p_0 = 0$, and $p_M = 0$. Thus, all E_m and F_m can be determined, as well as R_m and S_m . All values of p_m and q_m may also be calculated, and new values of the variables obtained because

$$u_m^{n+1} = p_m + u_m^n \quad (27)$$

$$w_m^{n+1} = q_m + w_m^n \quad (28)$$

The calculational processes are repeated until u and w are evaluated at all spatial points for the particular time of interest. Once the concentration distribution is known, then the flux through the material, the quantity retained in it [both in solution (u) and in traps (w)], and the total quantity that has permeated may be calculated.

DEMONSTRATING THE MATHEMATICAL MODEL

The accuracy and convergence of the techniques involving this application of finite difference methods to the solution of differential equations was demonstrated as follows. Convergence depends in part on the ratio $\Delta\tau/(\Delta X)^2$ and occurs more rapidly as this ratio decreases. For simple cases, a value of 1 or less is usually small enough to cause convergence in a reasonable time.² Unfortunately, for non-linear equations, such as the one considered here, there are no generally valid theorems to guide selection of the ratio $\Delta\tau/(\Delta X)^2$ or the size of the intervals. If too large a value is taken, the calculated values oscillate or diverge at successive stages. This possible effect was examined by calculations with different values of $\Delta\tau/(\Delta X)^2$. With $\Delta\tau/(\Delta X)^2 = 2, 1, \frac{1}{2}$, and $\frac{1}{4}$, a given set of values of the parameters λ, μ , and ν , and with $\theta = 0.500$, the calculated values for $u(X, \tau)$ and $w(X, \tau)$ agreed in all cases, thereby demonstrating the stability of the technique.

Accuracy of a finite difference technique depends upon the size of the intervals $\Delta\tau$ and ΔX . Accuracy for the present case was determined by selecting three different values of ΔX (0.005, 0.01, and 0.02), and the corresponding value of $\Delta\tau$ was established by keeping the ratio $\Delta\tau/(\Delta X)^2 = \frac{1}{2}$. Again the calculated values of $u(X, \tau)$ and $w(X, \tau)$ agreed to within several parts in 10,000. Based on the above tests of the technique, values of $\theta = 0.5$, $\Delta X = 0.01$, and $\Delta\tau/(\Delta X)^2 = \frac{1}{2}$ were used in subsequent calculations.

APPLICATION OF THE MATHEMATICAL MODEL

Permeation rates have been estimated from computer-generated tables of solutions to the difference equations for a number of combinations of the parameters λ , μ , and ν . Results of some representative calculations are illustrated in Figure 1, which compares permeation rates as a function of time for diffusion with trapping to the results of simple diffusion theory.

Although only a small portion of the possible range of combinations of λ , μ , and ν have been examined so far, several general observations appear to hold:

- o Permeation rates in the presence of trapping are always less than for simple diffusion at a given time.
- o The shape of the curves depends in a complex manner upon the selection of values for λ , μ , and ν .
- o Results reduce to those for simple diffusion if $\lambda = \mu = \nu = 0$ and reduce to the case of diffusion with chemical reaction if $\mu \neq 0$. Whether there is a unique solution (set of values of λ , μ , and ν) for a given experimental curve is yet to be established.

EXPERIMENTAL METHOD

Deuterium permeation through high-purity copper was measured for temperatures between 270 and 450°C. The specimens were cut from 0.0254-cm-thick (0.010 in.) copper foil cold-rolled from VP Grade copper by the Materials Research Corporation. The principal impurities listed by the supplier were: Zn <10 ppm, Al ~5 ppm, Ag ~3 ppm, O₂ ~2 ppm, H₂ ~1 ppm, and Si ~2 ppm. Purified deuterium at ~1 atm pressure was applied to one side of the foil, and permeation rates were measured with a leak detector that was periodically calibrated against a standard deuterium leak. For comparison with theoretical curves, the experimental data were plotted against reduced time, Dt/a^2 . In these calculations, the lattice diffusivity of deuterium in copper was taken from the data of Eichenauer, Löser, and Whitte.¹⁰

DISCUSSION

Diffusivity, $D^*(\text{cm}^2/\text{sec})$, of hydrogen in a metal may be calculated from the measured transient permeation rate from the relation

$$P_t/P_\infty = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-D^*n^2\pi^2t/a^2) \quad (29)$$

where P_t and P_∞ are the measured permeation rates, i.e., hydrogen fluxes on the zero pressure side of the foil, at time t (sec) and at steady state, respectively, and a is the foil thickness (cm). A similar equation describes gas evolution from a foil following

steady state permeation. If the basic assumptions in the derivation of the equation are satisfied by the experiment, the magnitude of D^* is independent of P_t/P_∞ and is equal to the lattice diffusivity, D , in the metal. This result is not obtained, however, in the case of deuterium permeation through copper.

If simple diffusion controlled the deuterium permeation and evolution rates, both experimental curves should lie together on the theoretical curve given by Equation 29. This was not the case, however, as illustrated by the data for the experimental run at 322°C in Figure 2. Neither of the experimental curves match the shape of the theoretical curve, a behavior that is consistent with the hypothesis that reversible trapping occurs in copper. Permeation curves at other temperatures were similar. If irreversible trapping occurred, for example by the reaction between deuterium and oxygen,³ the evolution curve should lie above the theoretical curve for all values of Dt/a^2 , and the permeation curve should lie below it. Comparison of the permeation curve (Figure 2) with Figure 1 suggests that a model of reversible trapping with $N \sim C_0 \sim 5 \times 10^{16}/\text{cm}^3$

$$\rho \sim 4 \times 10^{-3} \text{ (sec}^{-1}\text{)} \quad \text{and} \quad \kappa \sim 10^{-19} \text{ cm}^3/\text{atm-sec}$$

may reasonably represent the case for cold-rolled copper at 322°C. These values are equivalent to values for λ , μ , and ν of about 5. Such estimates are not accurate but indicate the magnitudes that are involved.

Diffusivities calculated by Equation 29 varied with P_t/P_∞ for both permeation and evolution, as shown in Figure 3. Generally the highest diffusivities were near steady-state ($P_t/P_\infty \rightarrow 1.0$). Furthermore, the diffusivities obtained in this work are less than those calculated from outgassing experiments on high-purity

single crystals of copper (Reference 10 and 11 and Figure 4), a result that is probably generally true if results of outgassing of saturated specimens and permeation experiments were compared.

In the case of α -iron where trapping is more pronounced, $N = 10$ to $100 C_0$.⁵ Experimental investigations currently in progress at the Savannah River Laboratory indicate that hydrogen and deuterium trapping are also observed in other metals such as silver and gold. These experiments and further testing of the method of solution of the differential equation are continuing.

CONCLUSIONS

Solutions to the non-linear partial differential equations formulated by McNabb and Foster⁸ for diffusion-plus-trapping may be obtained approximately by finite-difference methods for boundary conditions of practical interest. For the specific case of permeation, the solutions developed here appear stable over the limited range of the parameters (λ , μ , ν) that have been studied to date.

Permeation experiments on cold-worked high-purity copper suggest that reversible trapping occurs. The results fall within the range of behavior predicted by the McNabb and Foster model and lead to estimates of trap density of $N \sim C_0$ and the ratio $N\kappa/\rho \sim 1.0$ at 322°C.

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AES:sce

a) Equal values of parameters

b) Increasing trap density with constant trap and release rates

Figure 1. Representative Permeation Curves for Diffusion With Reversible Trapping

Figure 2. Relative Permeation Rates of Cold-Rolled Copper Foil at 322°C During Rise to Steady-State and Evolution After Permeation

a) Deuterium Permeation
(rise to steady state)

b) Deuterium Evolution
(decline from steady state)

Figure 3. Deuterium Diffusivity in Cold-Rolled Copper

Figure 4. Temperature Dependence of Deuterium Diffusivity in Cold-Rolled Copper