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H diffusion through partially internally oxidized Pd-alloy membranes

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Abstract

The H flux (J) has been measured through multilayer membranes of Pd and Pd–Al alloy prepared by internal oxidation of the alloy. A plot of $1/J$ against thickness of the Pd layers, $2d_{\mathrm{Pd}}$, is linear for a series of different $2d_{\mathrm{Pd}}$ values. This justifies assumptions of the model used to derive the relation between $1/J$ and $2d_{\mathrm{Pd}}$. D_{H} for Pd and the alloy can be obtained from intercepts of the plot using known p_{H_2}–H content isotherms. Since it has been shown that internal oxidation leads to more reproducible and poison-resistant Pd based membranes, the multilayer technique is an alternate way to obtain D_{H} for Pd alloys.

Keywords: Hydrogen diffusion; Multilayers

1. Introduction

In 1998 Kirchheim et al. remarked that “to their knowledge, experimental results on the diffusion of hydrogen through multilayers have not yet been reported” [1]. Their research dealt with diffusion through ultra-thin multilayers of Nb/Pd which they followed electrochemically using a time-lag method. Their results were somewhat uncertain in that no final conclusion about any effect of the internal interfaces could be reached. Very recently Yamakawa et al. [2] investigated Pd/Fe and Pd/Ni multilayers at 378–625 K and found no strong influence of the interfaces, however, there was grain boundary diffusion for the Pd/Ni layers and retardation, possibly due to dislocation trapping. Takano et al. [3] studied H diffusion through thin layers of Pd, Ni, or Cu deposited electrochemically on Fe and concluded that complications are introduced by thin films perhaps H trapping at vacancies as the thickness of the layer decreases to very small values. Holleck [4] measured H diffusion through mm thick $\mathrm{Pd}_{0.75}\mathrm{Ag}_{0.25}/\mathrm{Ta}/\mathrm{Pd}_{0.75}\mathrm{Ag}_{0.25}$ layers in the gas phase from 540 to 873 K and determined $D_{\mathrm{H,Ta}}$ from the overall diffusion constant and the known $D_{\mathrm{H,alloy}}$; he concluded that the interface did not play a significant role at these temperatures. As in Holleck’s work, the present research does not concern very thin multilayers but macroscopic ones, in this case, prepared by internal oxidation. The measurements will be carried out at a lower temperature than Holleck’s and with a variety of layer thicknesses. Most previous investigations have employed electrochemical time-lag methods [1,3,5,6] at ambient temperature and have assumed that the solubilities at the interfaces are in the ideal range. To our knowledge, an investigation of diffusion through layers prepared by internal oxidation has not been carried out.

Partial internal oxidation of Pd–M alloys leads to outer layers of Pd containing M oxide precipitates whilst the inner layer remains unoxidized Pd–M alloy. The alloy employed in this research is $\mathrm{Pd}_{0.96}\mathrm{Al}_{0.04}$ which was chosen because the authors have had extensive experience with its internal oxidation [7,8] and it has been shown that internally oxidized Pd–Al alloys are more resistant to poisoning by CO than pure Pd [10]. The specific Al content was chosen in order for it to be large enough for the alloy to have a significantly lower permeability than Pd but small enough

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to internally oxidize. The diffusion results may give some information about internal oxidation.

2. Experimental

The $Pd_{0.96}Al_{0.04}$ alloy membranes were prepared by arc-melting, rolling to the appropriate size and subjecting to internal oxidization in the atmosphere at ≈950–1000 K. The approximate extent of internal oxidation was followed by measuring the weight gain at frequent intervals. The final percent internal oxidation was determined more accurately by weighing after a brief heating of the membrane at 1123 K and quenching into cold water in order to decompose any PdO in the outer layers. The membranes were mounted in a Cajon fitting and heated to the desired temperature. The flux was determined from the fall of p_{H_2} with time on the upstream side of a known volume, 0.609 dm^3. The downstream side was evacuated continuously during the flux measurements. The fluxes were measured continuously over a period of 30 min and the steady state was established almost immediately for all the membranes.

3. Determination of diffusion constants in multilayers from the flux

Internal oxidation converts the Pd–M alloy into a Pd/M-oxide (e.g., Al_2O_3) composite with nano-sized precipitates [7–9]. After internal oxidation, a Pd–M membrane consists of two outer layers of a Pd/M-oxide composite, consisting of nanoparticulate metal oxide particles embedded in a pure Pd matrix, of equal thickness enclosing the inner, unoxidized layer of the alloy (Fig. 1). Thus when this is employed as a membrane, the H must permeate through three layers and two internal interfaces. It has been shown that dissolved H is trapped at the internal Pd/M-oxide interfaces but these traps are filled at very low p_{H_2} and thereafter play no role in the diffusion or solubility of H in the Pd matrix [9].

Eq. (1) expresses the equality of the steady-state fluxes through the three layers

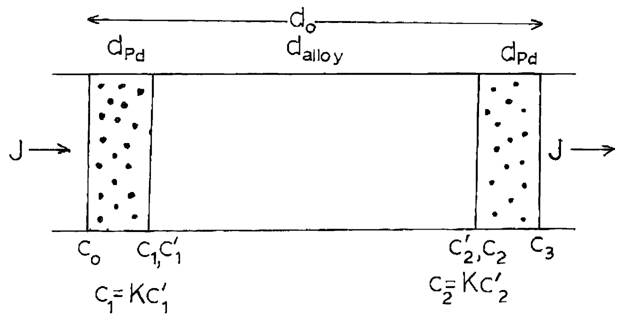

Fig. 1. Schematic representation of a partially internally oxidized Pd–M alloy where c_1 and c'_1 are the H concentrations in the Pd/M-oxide composite and in the alloy at interface 1, respectively. Similar designations are for interface 2. Concentration c_0 is given from the isotherm corresponding to $p_{H_2} = 0.05$ MPa (upstream) and $c_3 = 0$.

$$\begin{aligned} J &= D_{H,Pd}(c_0 - c_1)/d_{Pd} \\ &= D_{H,alloy}(c_1/K_1 - c_2/K_2)/d_{alloy} = D_{H,Pd}c_2/d_{Pd}, \end{aligned} \tag{1}$$

where $D_{H,Pd}$, $D_{H,alloy}$ are the H diffusion constants in the oxidized layer matrix (Pd) and the unoxidized alloy, respectively. The concentrations, c_i, are in mol H/cm^3 and are defined in Fig. 1. The H concentration in Pd at the upstream side, c_0, is obtained from the isotherm for Pd–H and p_{H_2} (upstream); it need not be in the ideal range. Because the downstream side of the membrane is continuously evacuated, $c_3 = 0$. The thicknesses, d_{Pd}, d_{alloy}, refer to an outer Pd layer and to the inner unoxidized alloy, respectively (Fig. 1). They are related by $d_0 = 2d_{Pd} + d_{alloy}$ where d_0 is the total thickness of the membrane and the (fraction internal oxidation) $\times d_0 = 2d_{Pd}$. K_1 and K_2 are the ratio of the H concentrations in Pd (the Pd/M-oxide composite) to that in the alloy at interfaces 1 and 2, respectively (Fig. 1). Solving Eq. (1) for $1/J$ gives Eq. (2)

$$\begin{aligned} 1/J = K_1 d_0/(c_0 D_{H,alloy}) + (2d_{Pd}/c_0)[(1/2D_{H,Pd})(1 + K_1/K_2) \\ - K_1/D_{H,alloy}]. \end{aligned} \tag{2}$$

If $K_1 = K_2 = K$, Eq. (2) reduces to Eq. (3),

$$\begin{aligned} 1/J = Kd_0/(c_0 D_{H,alloy}) + (2d_{Pd}/c_0)[(1/D_{H,Pd}) \\ - (K/D_{H,alloy})]. \end{aligned} \tag{3}$$

If Eq. (3) is valid, plots of $(1/J)$ against $2d_{Pd}$ should be linear and $D_{H,Pd}$ and $D_{H,alloy}$ can be obtained from the inter-

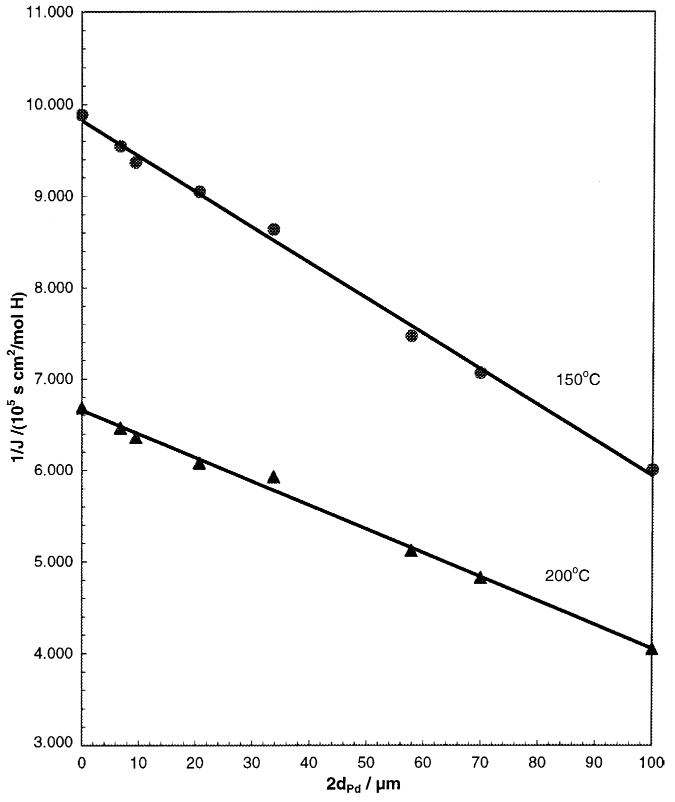

Fig. 2. Plot of $1/J$ against $2d_{Pd}$ for internally oxidized $Pd_{0.096}Al_{0.04}$ membranes at 423 and 473 K.