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H Diffusion through Partially Internally Oxidized Pd-alloy Membranes (U)

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Introduction

In 1998 Kirchheim *et al* remarked that “to their knowledge, experimental results on the diffusion of hydrogen through multi-layers have not yet been reported” [1]. Their research dealt with diffusion through ultra-thin multi-layers 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 $Pd_{0.75}Ag_{0.25}$/Ta/ $Pd_{0.75}Ag_{0.25}$ layers in the gas phase from 540-873 K and determined $D_{H,Ta}$ from the overall diffusion constant and the known $D_{H,alloy}$; he concluded that the interface did not play a significant role at these temperatures. As in Holleck’s, the present research does not concern very thin multi-layers 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 $Pd_{0.96}Al_{0.04}$ 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 [9]. 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 to internally oxidize. The diffusion results may give some information about internal oxidation.

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 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_{H2} 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.

Determination of Diffusion Constants in Multi-layers from the Flux

Internal oxidation converts the *Pd*-M alloy into a Pd/M-oxide (i.e. Al_2O_3) composite with nano-sized precipitates [7,8,10]. 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_{H2} and thereafter play no role in the diffusion or solubility of H in the Pd matrix [10].

Equation (1) expresses the equality of the steady-state fluxes through the three layers. By substituting in (1b) for c_1 from (1a) and c_2 from (1c), and then applying the layer thickness relationship, an equation appropriate for diffusion through the three layers formed from partial internal oxidation, where the outer two layers are identical, can be derived,

$$J=D_{H,Pd}\,(c_o-c_1)/d_{Pd}=D_{H,alloy}\,(c_1/K_1-c_2/K_2)/d_{alloy}=D_{H,Pd}\,c_2/d_{Pd} \qquad (1)$$

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 Figure 1. The H concentration in Pd at the upstream side, $c_{o,}$ is obtained from the isotherm for Pd-H and p_{H2} (upstream); it need not be in the ideal range. c_3=0 because the downstream side of the membrane is continuously evacuated. 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 $d_o = 2d_{Pd} + d_{alloy}$ where d_o is the total thickness of the membrane and the (% internal oxidation) x $d_o = 2d_{Pd}$. 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 equation (1) for 1/J gives equation (2)

$$1/J = K_1\, d_o/(c_oD_{H,alloy}) + (2d_{Pd}/c_o)[\,(1/2D_{H,Pd})(1 + K_1/K_2) - K_1/D_{H,alloy}\,]. \qquad (2)$$

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

$$1/J = K\, d_o/(c_oD_{H,alloy}) + (2d_{Pd}/c_o)[(1/D_{H,Pd}) - (K/D_{H,alloy})]. \qquad (3)$$

If equation (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 intercepts at $2d_{Pd}=d_o$ and at $2d_{Pd}=0$. Alternatively, the slope gives the value of $D_{H,Pd}$ because $D_{H,alloy}$ is known from the intercept. It will be established whether or not the data can be described by equation (3) and, if it does, this would support the assumptions about the internally oxidized layers. In this research d_{Pd} will be varied and thereby both $D_{H,Pd}$ and $D_{H,alloy}$ can be determined from the intercepts. Most investigations have employed only one set of layer thicknesses [1,2,4,5] and have determined one diffusion coefficient knowing the other one.

Results and Discussion

Results at 423 and 473 K for the partially internally oxidized $Pd_{0.96}Al_{0.04}$ alloy membranes are shown in Figure 2 for $p_{H2,upstream}=0.05$ MPa. The greatest % internal oxidation of a $Pd_{0.96}Al_{0.04}$ membrane shown on the Figure is 69.9%. The experimental end points of the straight line in Figure 2 are pure Pd and the unoxidized $Pd_{0.96}Al_{0.04}$ alloy membrane. The data give a good linear fit to equation (3) and the intercept at $2d_{Pd}=d_o$, gives $D_{H,Pd}$, i.e., $(1/J) = d_o/c_oD_{H,Pd}$ and at $2d_{Pd}=0$, $(1/J)= d_o/c'_oD_{H,alloy}$ which are both independent of K where $c^{\bullet}_o$ is the H concentration for equilibrium with the alloy at $p_{H2}=0.5$ MPa (423 or 473 K). Thus an isotherm for the alloy is needed for the appropriate temperature.

In order to learn why the approximation $K_1=K_2=K$ appears to be valid, K_1 and K_2 can be calculated for various percents internal oxidation where the subscripts 1,2 indicate the internal interfaces (Fig. 1). In order to obtain K_1, K_2 the H concentrations at the interface must be known. The value of c_o is known from the isotherm for Pd and c_1 can be obtained from the first two terms in equation (1), $J=D_{H,Pd}\,(c_o-c_1)/d_{Pd}$, and c_2 can be obtained from the first and last terms, $J=D_{H,Pd}\,c_2/d_{Pd}$. $2d_{Pd}$ is known at any value of % internal oxidation from the relation: (% internal oxidation) x $d_o=2d_{Pd}$. From c_1 and c_2, c_1' and c_2' can be obtained from the isotherms, e.g., from c_1 the corresponding p_{H2} can be obtained from the isotherm for Pd and from this p_{H2} and the isotherm for the alloy, c_1' can be obtained. Thus K_1 and K_2 can be calculated at several values of % internal oxidation. It is seen in Table 1 that the values of K_1 and K_2 are essentially the same *even though the concentrations are not in the ideal range*. The concentrations do not have to individually follow Sieverts' law, $c=k\, p_{H2}^{1/2}$, as long as their ratios are constant.

For instance, for the 9.2% internally oxidized alloy, c_1 and $c_1^{\bullet}$ can be converted to $r_1=22.3 \times 10^{-3}$ (19.3×10^{-3}) and $r_1^{\bullet}=17.8 \times 10^{-3}$ (15.4×10^{-3}); the values with and without parentheses are the ideal and real values, respectively. Although the H contents are in the non-ideal range as seen by the difference in *r* values, the ratio of r_1 to $r_1^{\bullet}$ is the same as for the ideal case, i.e., the degree of non-ideality is similar for Pd and for the alloy at these low H contents. In some of the other studies of H diffusion through multi-layers it has been assumed that Sieverts' law holds but it is shown here that this is too restrictive and instead only the ratios of the concentrations at each interface must be equal.

Table 1

Values of c_i and c_i' in mol H/cm^3 and K at the Internal Interfaces of the $Pd_{0.96}Al_{0.04}$ alloy Membrane with p_{H2}=0.05 MPa (423 K)

% Int. Oxid	c_i	c_2	c_i'	c_2•	K_1	K_2
9.2	2.52×10^{-3}	2.1×10^{-4}	2.01×10^{-3}	1.7×10^{-4}	1.25	1.22
33.7	2.33×10^{-3}	4.0×10^{-4}	1.88×10^{-3}	3.38×10^{-4}	1.24	1.22
57.8	1.94×10^{-3}	7.9×10^{-4}	1.54×10^{-4}	7.1×10^{-4}	1.26	1.24
69.9	1.71×10^{-3}	1.02×10^{-3}	1.38×10^{-3}	0.82×10^{-3}	1.24	1.23

The good fit of the experimental data shows that the basic assumptions in the derivation of equation (3) are valid for H diffusion through these partially internally oxidized alloys, i.e., there is no resistance to H diffusion at the internal interfaces, the interfaces are reasonably sharp, diffusion of H through the Pd/M-oxide composite is the same as through Pd itself and $K_1 \approx K_2 = K$ independent of % internal oxidation.

Conclusions

H diffusion through internally oxidized $Pd_{0.96}Al_{0.04}$ alloy membranes agrees with the equation for hetero-layer diffusion with one constant, K, for the ratio of the concentrations at the interfaces and there is no evidence for any resistance to H diffusion through the internal interfaces formed from internal oxidation and the interfaces must be reasonably sharp to fit the model. Even though the concentrations are not in the ideal range, the ratios of the concentrations are the same as in the ideal range.

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References

[1] G. Schmitz, Ph. Kesten, R. Kirchheim, Q. Yang, *Phys. Rev. B,* **58** (1998) 7333.

[2] K. Yamakawa, M. Ege, M. Hirscher, B. Ludescher, H. Kronmüller, *J. Alloys Compounds*, **393** (2005) 5.
[3] N.Takano, Y. Murakami, F. Terasak, *Scripta Metall. Mat*., **32** (1995) 401.

[4] R. Ash, R. Barrer, J. Petropoulos, *Brit. J. Appl. Phys*., **14** (1963) 854.

[5] T. Tanabe, K. Sawada, S. Imoto, *Trans. Jpn. Inst. Met.,* **27** (1986) 321.

[6] R. Song, S. Pyun, *J. Electrochem. Soc***., 137** (1990) 1051.

[7] R. Balasubramaniam, R. Kirchheim, D. Wang, T. Flanagan, *J. Alloys Compounds*, **293-295** (1999) 306.

[8] D. Wang, H. Noh, S. Luo, T. Flanagan, J. Clewley, R. Balasubramaniam, *J. Alloys Compounds*, **339** (2002) 76.

[9] D. Wang, T. Flanagan, K. Shanahan, *J. Mem. Sci*., **253** (2005) 165.

[10] X-Y. Huang, W. Mader, R. Kirchheim, *Acta metal. Mater*., **253** (1991) 893.

Figures

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. Similar designations are for interface 2. Concentration c_o is given from the isotherm corresponding to p_{H2}=0.05MPa(upstream) and c_3=0.

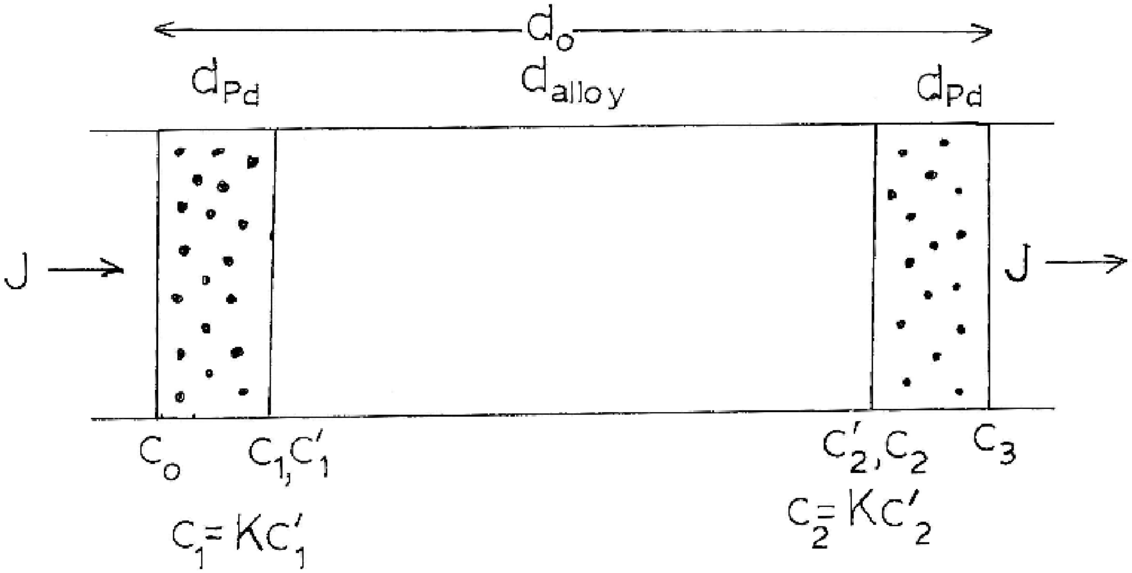

Fig. 2. Plot of 1/J against $2d_{Pd}$ for internally oxidized $Pd_{0.096}Al_{0.04}$ membranes at 423 and 473 K.