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Hydrogen permeation through magnesium

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Abstract

Hydrogen permeation characteristics have been investigated for pure magnesium membranes with a palladium overlayer using a gas permeation technique in the temperature range 473–493 K and in the hydrogen pressure range 0.1–10 kPa. For thicker specimens (thickness >2 mm), the permeation process was rate-controlled by the diffusion of hydrogen in bulk magnesium. The diffusion coefficient was determined to be $D = 1.54 \times 10^{-6} \exp(-24{,}100/RT)$ m^2 s^{-1}. The steady-state hydrogen permeability was determined to be $\Phi_{ss} = 2.77 \times 10^{-7} \exp(-35{,}700/RT)$ mol H$_2$ m^{-1} s^{-1} Pa$^{-1/2}$. D and Φ_{ss} were independent of the applied hydrogen pressure, suggesting that D is independent of hydrogen content and the solubility of hydrogen obeys Sieverts' law. The hydrogen solution constant K was determined to be $K = 1.8 \times 10^{-1} \exp(-11{,}600/RT)$ mol H$_2$ m^{-3} Pa$^{-1/2}$.

Keywords: Hydrogen; Permeation; Diffusion; Magnesium; Membrane

1. Introduction

Rechargeable hydrides based on magnesium alloys have long been expected to be promising candidates for hydrogen-energy applications. However, fundamental data on hydrogen behavior in magnesium alloys are quite scarce, especially for hydrogen diffusion. This is true even for pure magnesium, where few data have been reported [1,2]. In this study, the hydrogen permeation characteristics of pure magnesium were investigated to obtain hydrogen diffusion data.

2. Experimental

Disk samples of 12 mm diameter were sliced from a commercial magnesium ingot of 99.9% purity and then annealed under vacuum at 573 K for 3.6 ks. The average grain size was 1.5 mm. The samples were polished mechanically with emery paper and finished with 0.05 μm alumina abrasive. The samples were then quickly placed in an ultra-high-vacuum chamber for vacuum deposition. A palladium overlayer of 0.1 μm thickness was deposited on both sides as a hydrogen dissociation catalyst to provide membrane samples for hydrogen permeation. The thickness of the membranes ranged from 0.625 to 2.962 mm.

Hydrogen permeation was performed in an apparatus with an ultra-high-vacuum system in the temperature range 473–493 K using high pure hydrogen gas. Fig. 1 shows a schematic illustration of the experimental apparatus for hydrogen permeation. A knife-edge orifice with known conductance, C, was placed on the downstream side of the membrane sample. The hydrogen pressure applied on the upstream side of the membrane, P_1, was measured by an absolute pressure transducer. The hydrogen pressure on the upstream side of the orifice, P_2, and on the downstream side of the orifice, P_3, were measured by nude ionization gauges. The flux of hydrogen permeating through the

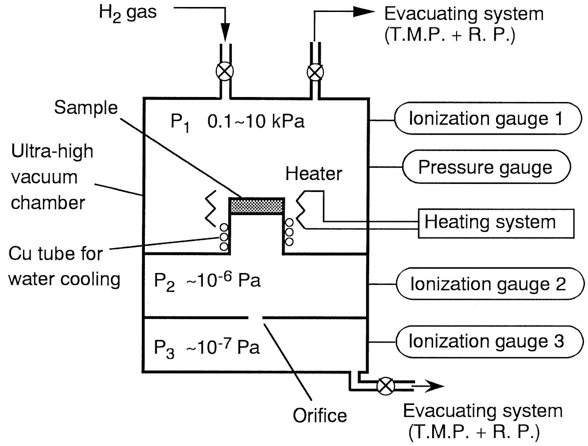

Fig. 1. Schematic illustration of the hydrogen permeation apparatus.

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membrane, J, is obtained from the orifice conductance, C, the pressure difference of P_2 and P_3, and the surface area of the membrane, A, as follows:

$$J = C(P_2 - P_3)/A \tag{1}$$

J is related to Φ by

$$J = \Phi(P_1^{1/2} - P_2^{1/2})/L \tag{2}$$

where L is the thickness of the membrane. The steady-state hydrogen permeability, Φ_{ss}, can be determined when sufficient time has passed from $t = 0$, and $P_2 - P_3$ saturates, by Eqs. (1) and (2). D can be determined from the breakthrough time, t_b [3], by the equation

$$D = L^2/2\pi^2 t_b \tag{3}$$

Prior to the measurement of magnesium membranes, hydrogen permeation was performed using a 0.5 mm thick palladium membrane as a standard sample, in order to calibrate ionization gauges 2 and 3 (see Fig. 1), and to ascertain the validity of applying Eqs. (1)–(3). The obtained values of Φ_{ss} and D showed fairly good agreement with literature data [4,5]; the difference was at most 10% for both Φ_{ss} and D. The ionization gauges were therefore used in as-provided condition in the following measurements. From Φ_{ss} and D, the hydrogen solution constant, K, on the upstream side surface of the magnesium membrane can be determined as

$$K = \Phi_{ss}/D \tag{4}$$

After $P_2 - P_3$, and hence J, reached a steady state, P_1 was instantly increased or decreased to another value to start the next measurement. At least five measurements were performed at distinct hydrogen pressures, P_1, at a certain temperature. Φ_{ss}, D and K were determined by averaging the values obtained for each run at each temperature.

Table 1
Measured breakthrough time

Sample thickness (mm)	Breakthrough time (s)		
	473 K	483 K	493 K
0.625	12.7	11.3	10.0
1.335	37.5	31.8	29.5
2.128	66.7	60.7	52.4
2.860	118.1	111.4	87.8
2.962	133.9	114.0	100.3

3. Results and discussion

Fig. 2 shows an example of the curves of $P_2 - P_3$ versus time, from which D and Φ_{ss} were obtained for the 2.128 mm thick membrane sample at 493 K. The typical permeation curve was obtained as follows: the curve shows a clear incubation time in the initial stage, then a region of constant gradient, and then finally becomes constant.

Table 1 lists the breakthrough times, t_b, for all the samples investigated. It is shown that t_b increases as the thickness increases, and decreases as the temperature increases. Fig. 3 shows the thickness dependence of the apparent diffusion coefficients, D_{ap}, obtained from Eq. (3) and the values of t_b listed in Table 1. For each tempera-

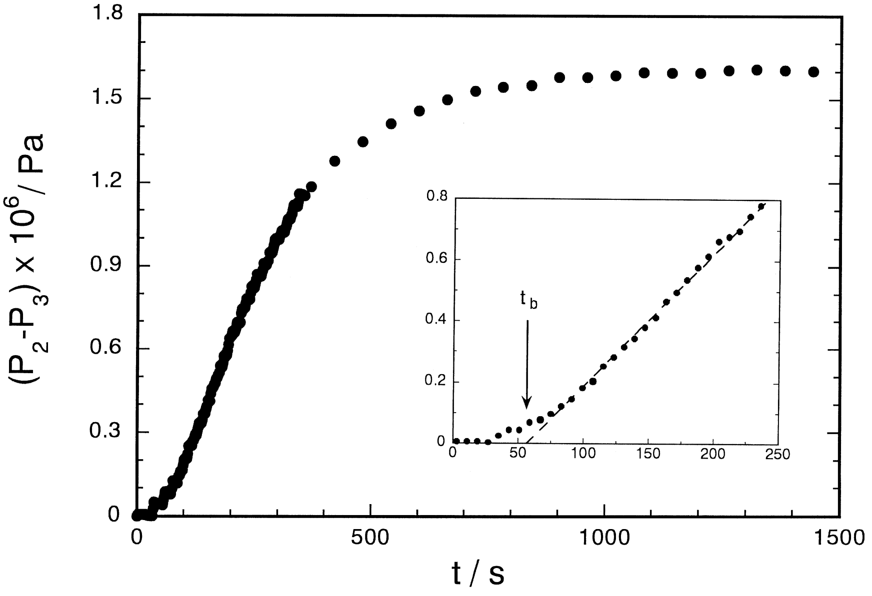

Fig. 2. Time dependence of $P_2 - P_3$ for a 2.128 mm thick membrane at 493 K.

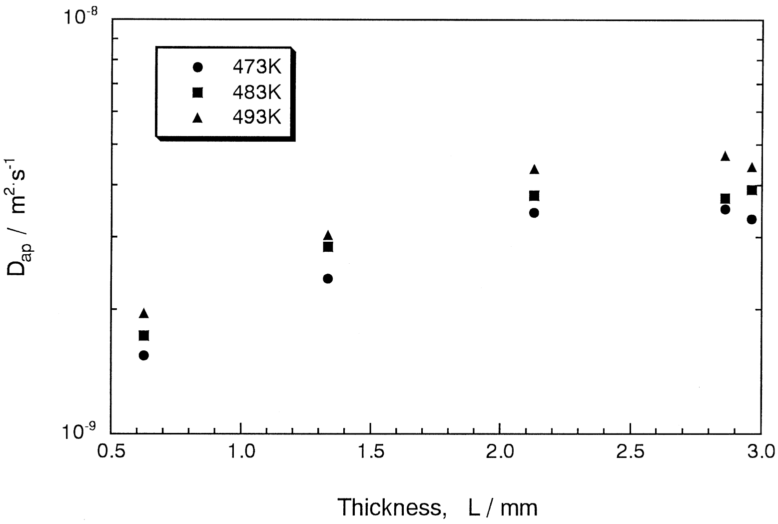

Fig. 3. Thickness dependence of the apparent diffusion coefficient of hydrogen, D_{ap}.

ture, D_{ap} increases as the thickness increases up to 2.128 mm, and then becomes constant at higher values of the thickness. In thinner samples, it is likely that the contribution of surface processes was significant in the permeation process, and hence D_{ap} was calculated to be low. The contribution of surface processes decreases as the thickness increases. For samples of 2.128 mm or thicker, the time for hydrogen permeation through bulk magnesium became sufficiently long, and the contribution of surface processes became negligibly small. In the following discussion of the hydrogen diffusion coefficient, *D*, averages for the thicker three membranes (see Table 1) are used exclusively.

The thickness dependence of Φ_{ss} showed a similar tendency to that of D_{ap}; Φ_{ss} increased as the thickness increased up to 2.128 mm, and then became constant at higher values of the thickness. Fig. 4 shows the thickness dependence of the hydrogen solution constant, *K*. Unlike D_{ap} and Φ_{ss}, *K* is independent of the thickness. This suggests that the effective surface area, which will affect the equilibrium hydrogen content, is apparently identical for all samples. This means that it is the kinetics of hydrogen that control the hydrogen permeation characteristics of the membranes investigated here.

Fig. 5 shows the hydrogen-pressure dependence of *D* and Φ_{ss} for a 2.128 mm thick membrane at 483 K. As can be seen, *D* and Φ_{ss} are independent of the applied hydrogen pressure, P_1, suggesting that *D* is independent of the hydrogen content, and the hydrogen solubility on the upstream side surface obeys Sieverts' law in the hydrogen pressure range investigated.

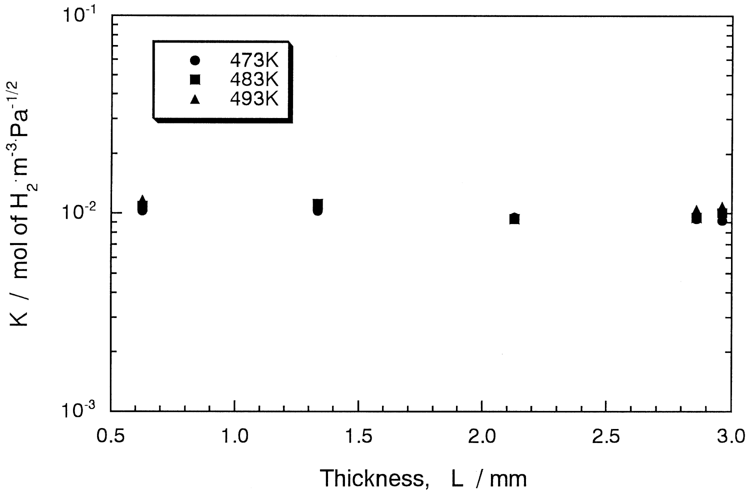

Fig. 4. Thickness dependence of the hydrogen solution constant, *K*.

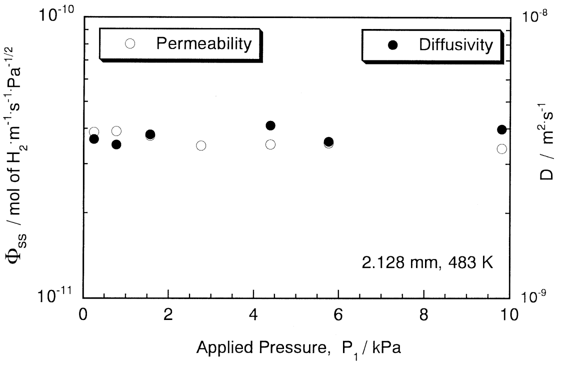

Fig. 5. Hydrogen-pressure dependence of the steady-state hydrogen permeability, Φ_{ss}, and the diffusion coefficient, D, for a 2.128 mm thick magnesium membrane at 483 K.

Figs. 6 and 7 show Arrhenius plots of D and Φ_{ss}, respectively. The least square fitting gives the equations

$$D = 1.54 \times 10^{-6} \exp(-24{,}100/RT) \qquad (5)$$

$$\Phi_{ss} = 2.77 \times 10^{-7} \exp(-35{,}700/RT) \qquad (6)$$

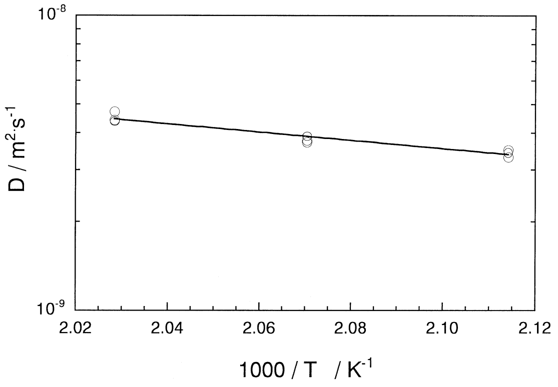

Fig. 6. Temperature dependence of the hydrogen diffusion coefficient, D, determined from magnesium membranes with thicknesses of 2.128, 2.860, and 2.962 mm.

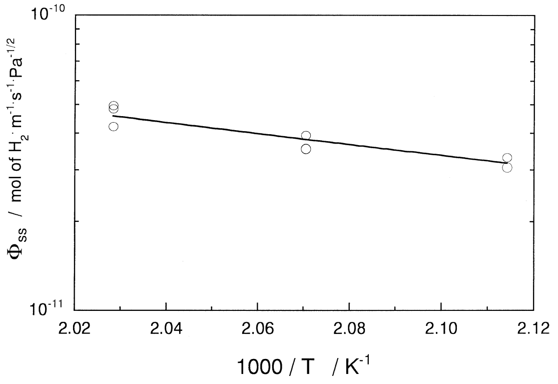

Fig. 7. Temperature dependence of the steady-state hydrogen permeability, Φ_{ss}, determined from magnesium membranes with thicknesses of 2.128, 2.860, and 2.962 mm.

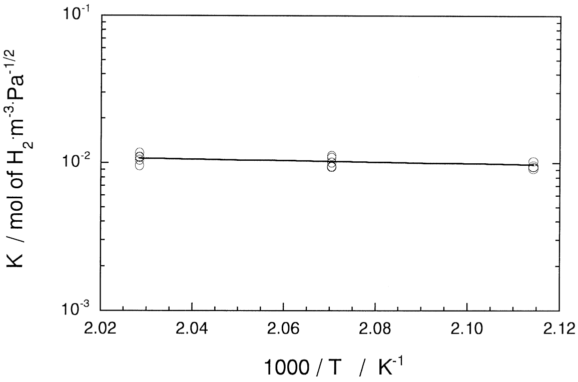

Fig. 8. Temperature dependence of the hydrogen solution constant, K, for all magnesium membranes investigated.

where D is in $m^2\ s^{-1}$, Φ_{ss} in mol $H_2\ m^{-1}\ s^{-1}\ Pa^{-1/2}$ and R in J $mol^{-1}\ K^{-1}$.

Fig. 8 shows the Arrhenius plot of K. As can be seen, the temperature dependence is small, and K decreases as temperature decreases. The latter fact means that hydrogen dissolves in magnesium endothermically. This tendency agrees well with previous work on hydrogen solution behavior in magnesium [6,7]. The least square fitting gives the equation

$$K = 1.8 \times 10^{-1} \exp(-11{,}600/RT) \qquad (7)$$

where K is in mol $H_2\ m^{-3}\ Pa^{-1/2}$. The resulting heat of solution (ΔH) of 0.5 mol H_2 is 11,600 J mol^{-1}.

Reports on hydrogen diffusion in magnesium are quite scarce. The only published report on the hydrogen diffusion coefficient was given by Rener and Grabke [1], where they determined the hydrogen diffusion coefficient in Mg–2 mass% Ce alloy by studying the growth rate of the hydride layer. They gave the diffusion coefficient as $D = 3.8 \times 10^{-6} \exp(-40{,}000/RT)\ m^2\ s^{-1}$. We believe that the present data given by Eq. (5) are the first data for the

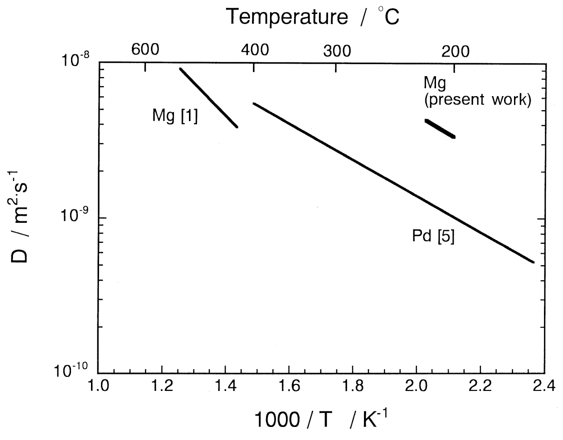

Fig. 9. Comparison of hydrogen diffusion data determined in the present work with data reported by Rener and Grabke [1]. Data for palladium [5] are also shown.

hydrogen diffusion coefficient in pure magnesium determined by a dynamic method. Fig. 9 compares the present data with the data reported by Rener and Grabke. Data for palladium [5] are also shown for comparison. The activation energy for hydrogen diffusion determined in the present work, 24.1 kJ mol^{-1}, is substantially smaller than the data reported by Rener and Grabke, 40.0 kJ mol^{-1}. The resulting value of D is significantly higher in this study. Concerning hydrogen mobility in magnesium, Tzanetakis et al. reported the activation energy to be 17 kJ mol^{-1} [2], which is rather close to the present data. It is surprising that the value of D determined in the present work is even higher than that for palladium. It is not clear at present why hydrogen diffusion in magnesium is so fast. It should be pointed out that hydrogen permeation experiments using single crystals and polycrystals with controlled grain size are important to fully understand hydrogen diffusion behavior in magnesium.

4. Conclusions

Hydrogen gas permeation was performed for palladium-plated magnesium membranes of different thicknesses. For thicker specimens (thickness >2 mm), the permeation process was rate-controlled by the diffusion of hydrogen in bulk magnesium. The diffusion coefficient was determined to be $D = 1.54 \times 10^{-6} \exp(-24{,}100/RT)$ m^2 s^{-1}.

Acknowledgements

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