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MEASUREMENT OF TRITIUM PERMEATION THROUGH RESISTANT MATERIALS NEAR ROOM TEMPERATURE

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ABSTRACT

To measure tritium permeation through low-permeability materials at 50-170°C, we use highly-sensitive liquid scintillation counting to detect the permeating tritium. To validate our method, we conducted extensive experiments with copper, for which much data exists for comparison. We report permeability of tritium through copper at 50, 100, and 170°C, and discuss details of the experimental technique. Further plans are outlined.

INTRODUCTION

Tritium permeation through materials used in tritium research systems and projected for use in fusion reactors poses continual problems with system utility and safety. Tritium is commonly used near room temperature, but there is very little data on permeation in this temperature range. In this paper we report results of an extensive study of copper, which is fairly low in permeability. Since there is much data on hydrogen permeation through copper, we selected it as a standard for validation of our experimental method and data analysis. We plan to next study a range of materials, including structural metals and coatings that can be applied to metals. Surface modifications of metals also offer promise of reduced tritium permeation, and ceramics are low-permeability materials for which little data exists at our temperatures. We also plan development of a tritium permeation model.

EXPERIMENTAL DESCRIPTION

Experimental Method

A sample membrane is held in a permeation cell with tritium gas on one side and triethylene glycol liquid on the other. As tritium permeates through the membrane, it exchanges with hydrogen in the triethylene glycol and is retained. Periodically a sample of glycol is withdrawn for tritium analysis by liquid scintillation counting. From the rate of tritium permeation into the glycol, we calculate the permeability of the sample and estimate the diffusivity using the time-lag permeation method.

Equipment

Permeation cells, shown in Figure 1, are constructed of type 304 stainless steel. Each sample disc is sealed in a cell with a copper gasket on each side; the gaskets have a sharp edge pressing on the sample disc to seal it, and are sealed to the cell body with standard knife-edge vacuum flanges. Tritium is contained in the volume of the valve body and flange, about 1 cm^3. The long reservoir contains triethylene glycol, typically 8 cm^3, and is sealed on the end with a high-temperature silicone-rubber septum. Liquid samples are taken with disposable syringes through the rubber septum.

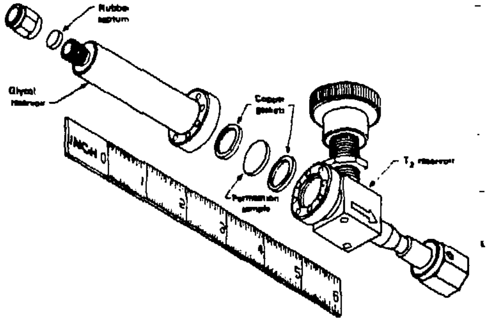

Figure 1. Permeation Cell Design

There are several advantages to this cell design. All of the components are inexpensive; therefore each cell is used only once and then discarded to prevent buildup of radioactive background. Any tritium leakage around the membrane or permeation through the edge of the membrane simply passes into the ventilated constant-temperature oven and is exhausted. Because the permeation cells are small, many samples can be run simultaneously -- up to 96 with our current equipment -- in contrast with mass spectrometer measurements which must be run serially.

Sample Preparation

Sample discs of two-cm diameter were cut from high-purity sheets (Aesar "Puratronic" grade) of the desired thickness. These were degreased with soap and water and then scrubbed with talc-like calcium carbonate powder to remove surface scale. Following a rinse with de-ionized water, the samples were ultrasonically cleaned with methanol and then dried. The samples were next sputter etched with a argon-ion bombardment in vacuum to provide a clean surface, and then sputter coated with a 500 or 1500Å palladium layer on both sides. The palladium layer serves two purposes: it prevents oxidation of the sample membrane by impurities in the tritium gas or by the triethylene glycol, and it catalyzes the isotopic exchange of tritium into the triethylene glycol liquid. Because the permeation of hydrogen through palladium is so rapid in comparison with copper (and all the materials of interest here), it has no effect on the rate of tritium permeation through the membrane.[1] The palladium-coated membranes were then mounted in the permeation cells for testing.

The purity of the membrane surface is critical to the accurate measurement of permeation, since a contaminated surface may impede permeation and cause an anomolously low permeation rate. To determine the surfaces cleanliness, we used Auger electron spectroscopy in conjunction with ion-beam sputtering to provide a depth profile of samples both before and after permeation experiments. With this technique, we could detect contamination of the permeation membrane that resulted from the cleaning or palladium-coating process, or that was formed during permeation. If we saw no oxide layer, we could be confident of the sample purity.

Procedure

To initiate a permeation experiment, the cell was assembled with the palladium-coated sample of interest (several samples were run at one time). Following a helium-leak check, the cell was evacuated overnight or longer to 10^{-5} Pa and then loaded with tritium. A sample of the tritium was taken for analysis by mass spectrometry. The loading pressure was selected so the pressure at the experiment temperature was 101 kPa. The cell was then weighed before and after addition of the triethylene glycol, an initial glycol sample was withdrawn for background determination, and the sample was placed in a constant-temperature oven for permeation. During the run, triethylene glycol samples were taken periodically. An amount of glycol equal to that removed was added to the cell after each sample so that the liquid amount in the cell remained unchanged. The triethylene samples were diluted in scintillation cocktail (Instagel) and counted in a Packard Tri-Carb Model 460 liquid scintillation counter. At the end of the run, the cell was weighed to check for loss of triethylene glycol, and the tritium analyzed for contaminant formation by mass spectrometry.

Data Analysis

The total tritium flux, calculated from the scintillation data, typically shows an accelerating permeation rate as the material becomes saturated with tritium which levels off when the material reaches an equilibrium content of tritium. The tritium permeability of the material can be calculated from this constant, steady-state permeation rate:

$$\text{rate} = \Phi\sqrt{\Delta P}\,A/l \qquad (1)$$

where

rate = steady state tritium flux, moles/s

Φ = tritium permeability, mole/m·s·Pa$^{1/2}$

ΔP = permeation driving pressure, Pa (for downstream pressure << upstream pressure)

A = sample surface area, m^2

l = sample thickness, m.

The permeation time lag, that interval during which tritium is building up in the material and permeation is not at steady state, can be estimated by extrapolation of the steady-state permeation data to zero flux; the diffusivity of tritium in the sample is proportional to this time lag:

$$\tau = l^2/6D \qquad (2)$$

where

τ = time lag, s

l = sample thickness, m

D = tritium diffusivity, m^2/s.

Since the tritium permeability is the product of diffusivity and solubility, the solubility of tritium in the sample is easily calculated from the permeability and diffusivity results. However, in many cases the time lag is very short in comparison with the experiment duration, and estimation of the diffusivity is not possible. (The estimate of diffusivity is considerably less accurate than the permeability measurement, since the relative error in intercept determination is many times larger than that in slope determination [2]).

RESULTS AND DISCUSSION

Purity of Palladium Coating

An Auger-spectroscopy depth profile of a typical palladium-coated sample is shown in Figure 2. The time to sputter through the palladium layer, 2200 s, represents a thickness of about 1500Å. There was only a trace amount of oxygen present in the palladium layer and none in the copper.

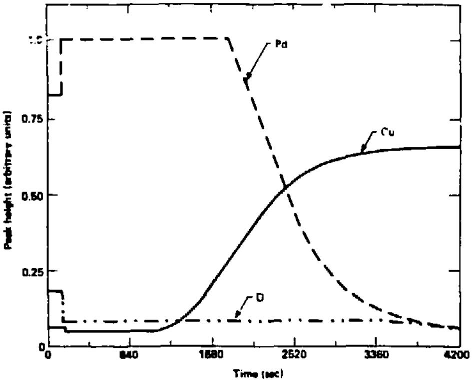

Figure 2. Ion-sputtered depth profile of typical copper permeation disc, using Auger electron spectroscopy. Pd-layer thickness is 1500 A; very little O is present

Typical Permeability Data

Data from a typical experiment is shown in Figure 3. The permeation rate is initially slow, but rapidly reaches the steady-state value shown by the least-squares line in Figure 3. The permeability shown in Figure 3 was calculated using Equation (1). Results for all experiments are summarized in Table 1.

Tritium Permeability at 50°C

Nine of the twelve experiments at 50°C gave quite consistent permeability values, but three of the runs gave significantly lower permeation rates. Auger analysis of

Table 1. Experimental measurements of tritium permeability through copper.

	temp	variables				permeability	diffusivity
Run	°C	A	B	C	D	mole/m·s·$Pa^{1/2}$	m^2/s
C-1	50	-	-	-	+	4.4×10^{-18}†	0.8×10^{-14}
C-2	50	-	-	+	+	0.55 " *	4 "
C-3	50	-	+	-	+	3.8 " †	0.7 "
C-4	50	+	-	-	+	4.4 " †	10 "
C-5	50	-	+	+	+	3.9 " †	0.4 "
C-6	50	+	-	+	+	2.6 " †	6 "
C-7	50	+	+	-	+	3.2 " †	1 "
C-8	50	+	+	+	+	5.2 " †	3 "
C-9	50	-	-	-	+	3.6 " †**	2 "
C-10	50	+	-	-	+	3.3 " †	1 "
C-11	50	-	-	+	+	0.20 "	-
C-36	50	-	+	+	+	0.36 " *	4 "

† average value from runs marked†: $3.8\pm0.8\times10^{-18}$
* oxygen present in Pd layer
** no oxygen present in Pd layer

C-13	100	-	-	-	+	3.3×10^{-18}††	-
C-14	100	-	-	+	+	3.1 " ††	-
C-15	100	-	+	-	+	3.5 " ††	-
C-16	100	+	-	-	+	0.08 "	-
C-17	100	-	+	+	+	leaked	-
C-18	100	+	-	+	+	0.09 "	2×10^{-14}
C-19	100	+	+	-	+	49 "	1×10^{-14}
C-20	100	+	+	+	+	0.9 "	-
C-21	100	-	-	-	+	2.8 " ††	-
C-22	100	+	-	+	+	0.1 "	-
C-23	100	-	-	+	+	4.3 " ††	-
C-24	100	-	+	+	+	2.9 " ††	-

††average value from runs marked ††: $3.3\pm0.6\times10^{-18}$

C-25	170	-	-	-	-	0.2×10^{-17}÷	-
C-26	170	-	-	+	+	9.2 " †††	-
C-27	170	-	+	-	+	7.7 " †††	-
C-28	170	+	-	-	+	9.2 " †††	-
C-29	170	-	+	+	-	0.2 " ÷÷	-
C-30	170	+	-	-	-	1.4 " ÷÷	-
C-31	170	+	+	+	-	0.02 " ÷	-
C-32	170	+	+	+	+	0.8 " ÷	-
C-33	170	-	-	-	-	0.3 " ÷	-
C-34	170	+	-	-	+	10.7 " †††	-
C-35	170	-	-	+	+	3.4 " ÷	-
C-12	170	-	+	+	-	1.5 " ÷÷	-

†††average value from runs marked †††: $9.2\pm1.2\times15^{17}$
÷ tritium leaked during run; measured value is low
÷÷ gas is primarily H_2 due to T_2/H_2 exchange; measured value is low

A = sample thickness; - = 0.25mm, + = 0.5 mm
B = Pd thickness; - = 500A, + = 1500 A
C = glycol liquid volume/vapor volume; - = 8cc/8cc, + = 22 cc/1cc
D = tritium pressure; - = 4 kPa, + = 101 kPa

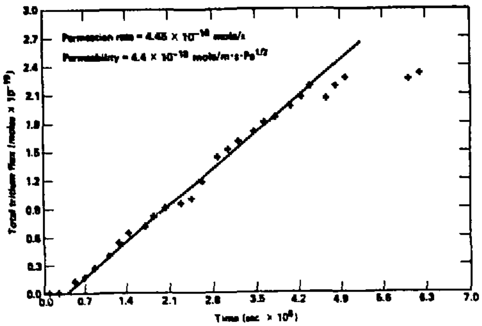

Figure 3. Permeation data for run C-4, copper at 50°C. Sample thickness 0.50 mm, diameter 16.0 mm, tritium pressure 101 kPa.

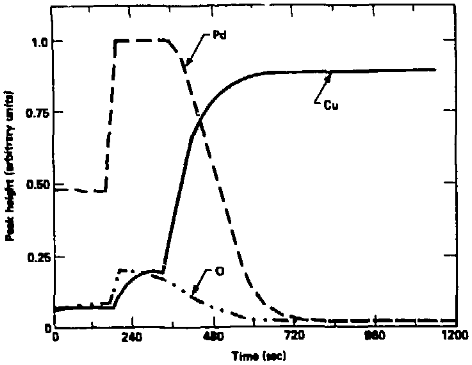

Figure 4. Ion-sputtered depth profile of copper permeation disc after run C-2, using Auger electron spectroscopy; O is present in Pd layer.

two of these samples (one of which is shown in Figure 4) showed much more oxygen in the palladium layer than was present in the pure coating in Figure 2. Analysis continues, but it appears that impurities in the palladium layer caused the low permeability in three samples (C-2, C-11, C-36). Without those three runs, the remaining runs averaged 3.8 ±0.8x10^{-18} mole/m·s·Pa$^{1/2}$.

Diffusivity measurements show a large spread; in one case, Run C-11, steady-state permeation was reached almost immediately, so calculation of diffusivity was impossible. We extrapolated data from Eichenbauer[3], Caskey[4], Belyakov[5], and Perkins[6] and estimated the diffusivity as D=3 x 10^{-13} m^2/s at 50°C. This is much higher than any of the values in Table 1, and is so fast that measurement would not be practical with our method and sample thickness (attainment of steady- state permeation would be virtually immediate). The slower values measured in most of our experiments presumably reflect non-ideal surface or bulk behavior (e.g. surface barriers, bulk trapping) in our samples.

In all runs at 50°C, tritium permeation tailed off to lower rates after long times, as shown in Figure 3. The cause is unknown, but Coronado has suggested that buildup of tritiated hydrocarbons in the gas (from the action of tritium radioactivity on stainless-steel contaminants) may poison the palladium surface and retard permeation.[7] With mass spectrometry we have indeed seen formation of tritiated methanes during permeation runs (typically 1-5 mol% of the final gas was isotopically-mixed methane) and plan to study this issue further.

Tritium permeability at 100°C

With copper samples of 0.25 mm thickness, the permeability measurements were quite consistent, yielding 3.3±0.6x10^{-18}. However, the 0.5 mm samples showed a wide variation in results, from 0.08-49 x 10^{-18}. Most samples showed a rapid initial permeation consistent with that through the thinner samples, but the permeation rapidly slowed to the rates shown in Table 2. Run C-19 showed quite low permeation initially, then gradually broke through to a very rapid permeation rate. The slow permeation probably reflects a poisoning of the sample -- Auger analysis is in progress to study this question. The rapid permeation of sample C-19 was perhaps caused by a fault in the metal opening up a rapid leak path. The permeability values measured with the thinner samples represent our best consistent data at 100°C. The diffusivity of tritium at 100°C is so fast that steady state should be reached essentially immediately; this was observed in all runs except C-18 and C-19.

Tritium Permeability at 170°C

In this series we varied the initial tritium pressure. Five of the samples developed gas leaks during the experiment and were ruined (mass spectrometry analysis of the gas after permeation showed air present in the gas). In addition, in the three other runs with low tritium pressure (4 kPa), isotope exchange between tritium gas and hydrogen in the stainless steel resulted in the gas containing 60-70% H_2 at the end of the runs. This exchange occurred in all runs, but for experiments at higher tritium pressures the amount of hydrogen exchanged into the gas was still much less than the tritium present. Because of this exchange, all runs with 4 kPa of tritium were invalid. The four runs with 101 kPa tritium that did not leak provide our measurement at 170°C. The tritium permeability is $9.2 \pm 1.2 \times 10^{-17}$ mole/m·s·pa$^{1/2}$.

Other Experimental Considerations

The experimental design comprised a factorial test of the significance of sample thickness, palladium thickness, and triethylene glycol volume. Although complete data were not obtained at 170°C, and there was apparent contamination of the thick copper samples at 100°C, we conclude that none of these effects were significant. The first two indicate that we were measuring bulk permeation instead of surface effects; the third shows that the isotopic exchange of tritium into the glycol is rapid and complete. The solubility of hydrogen in triethylene glycol is low;[8] if tritium were dissolving instead of isotopically exchanging with the glycol, variation of the liquid-to-vapor volume ratio would have an effect on the amount dissolved and subsequently detected. If the isotopic exchange were slow, then an increase in glycol volume would allow a longer tritium residence time and hence a more complete exchange; if this were the case, then runs with higher glycol liquid volume would have given higher measured permeabilities. Since no effect of glycol volume was seen, we conclude that tritium exchange into the glycol liquid is indeed rapid and complete.

Corrosion of the palladium layer or of the copper gaskets by the triethylene glycol could cause degradation of the permeation sample surface and hence invalidate the measurements. However, atomic absorption anaylsis of glycol and Auger analysis of sample discs after permeation showed that there was no significant corrosion.

In all runs we observed buildup of some H_2 in the tritium from exchange of tritium with hydrogen in the stainless steel cell. In all cases except the low-pressure runs at 170°C, the fraction of tritium replaced by hydrogen was low. For the low-pressure runs at 170°C, most of the tritium was replaced by hydrogen, and the runs were not valid. In all runs we also observed formation of hydrocarbons from the reaction of tritium with organic impurities adsorbed on the stainless steel cells and with carbon contained in the steel. At 50 and 100°C, the tritium contained, on average, 3% isotopically-mixed methanes after an experimental duration of 81 days. At 170°C the hydrocarbon level was somewhat higher, about 6% after 58 days.

Temperature Dependence of Permeability

The permeability of copper to hydrogen and deuterium has been measured by many investigators at higher temperatures[3-6,9-15]; one measurement of tritium permeation has been made.[4] The results, converted to tritium permeability by the square root of the inverse ratios of gas molecular weights,

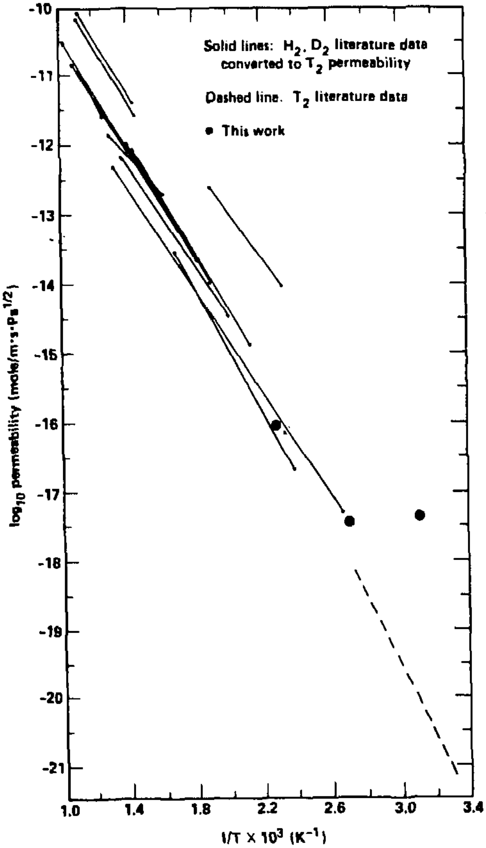

Figure 5. Tritium permeability through copper: literature values and experimental results.

are shown in Figure 5. From this data, the average activation energy for permeation is about 74 kJ/mole. Our measurements are shown as points in Figure 5. The agreement withprevious measurements is reasonable at 100 and 170°C, although our measured activation energy for tritium permeation is somewhat less, about 65 kJ/mole. The permeability at 50°C, essentially equal to that at 100°C, is much faster than expected from high-temperature results and from the one tritium measurement in that range. Most effects of sample impurities or gas contamination would result in a retardation of permeation, not an enhancement, so those are not likely explanations for the observed high rate; these may have contributed to the low permeation rates observed in the one study at low temperature. Work continues to study this apparently anomalous temperature behavior.

Sensitivity of Technique

We have measured tritium fluxes of 10^{-18} mole/s in preliminary work with other materials (100-fold less than fluxes in this work); fluxes many orders of magnitude lower are within our sensitivity limit. In comparison, the one experimental measurement of hydrogen permeation through copper at 375 K (with the slowest measured rate) was done with a mass spectrometer with a sensitivity of 10^{-15} mole/s.[4] Thus the sensitivity of our liquid scintillation technique is perhaps a million-fold greater than typical mass spectrometric techniques.

CONCLUSIONS

We have established the validity of our liquid scintillation technique for measurement of tritium permeation through low-permeability materials by an extensive series of tests with copper. Measurements at 100 and 170°C show good agreeement with results in the literature; there is scant data to compare with the results at 50°C. Several experimental parameters have been shown to be insignificant to the measured permeation rates. Work continues to understand the observed rapid permeation at 50°C. We will conduct studies on additional materials, and plan to develop a model of the permeation processes occurring.

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