



ca9110991

**DEUTERIUM PERMEATION AND
DIFFUSION IN HIGH PURITY
BERYLLIUM**

CFFTP-G-9013
May, 1990

**DEUTERIUM PERMEATION AND
DIFFUSION IN HIGH PURITY
BERYLLIUM**

CFFTP-G-9013

May, 1990

**'C-Copyright Ontario Hydro, Canada 1990. Enquiries
about Copyright and reproduction should be addressed
to:**

**Program Manager, CFFTP
2700 Lakeshore Road, West
Mississauga, Ontario
L5J 1K3**

Deuterium Permeation and Diffusion in High Purity Beryllium

E. Abramov*, M.P. Riehm, D.A. Thompson

Department of Engineering Physics, McMaster University

Hamilton, ONTARIO, L8S 4M1, CANADA.

and W.W. Smeltzer

Department of Metallurgy and Material Science, McMaster University,

Hamilton, ONTARIO, L8S 4M1, CANADA.

ABSTRACT

The permeation rate of deuterium through high-purity beryllium membranes was measured using the gas-driven permeation technique. The time-dependent and the steady-state deuterium flux data were analyzed and the effective diffusivities of the samples were determined. A multilayer permeation theory was used in order to eliminate the surface oxide effects and the diffusion coefficients of the bulk beryllium were determined. The diffusion parameters obtained for the extra-grade beryllium samples (99.8%) are $D_0 = 6.7 \times 10^{-9}$ [m²/s] and $E_D = 28.4$ [KJ/mole]; and for the high-grade beryllium samples (99%) the parameters are $D_0 = 8.0 \times 10^{-9}$ [m²/s] and $E_D = 35.1$ [KJ/mol].

* Permanent Address: Nuclear Research Center Negev, P.O. Box 9001, Beer-Sheva, ISRAEL, 84190

1. Introduction

Recently, the subject of hydrogen isotopes, especially tritium, behavior in beryllium has attracted increased attention because of the potential use of beryllium as a neutron multiplier in various fusion device blanket designs.^[1] The low atomic number and good thermal properties of the beryllium also make it attractive for a limiter and/or wall coating material in existing and future fusion reactors.^[2] Recent tests conducted in the Joint European Tokamak (JET) strengthen this trend, as they confirm that the plasma performance is enhanced using beryllium tiles on the first wall.

However, relatively little information has been published on the diffusion, solubility and permeation of hydrogen isotopes in beryllium.^[3-8] Such measurements are, generally, very difficult to make and the analysis is complicated by trapping and surface effects. These difficulties, coupled with the problem of a wide variation of properties caused by even minor changes in sample parameters such as impurities (especially oxygen), preparation processes and surface condition, contribute to the fact that the data reported in the literature is inconsistent and confusing (see Table 1).

The purpose of the present study is to measure the permeability and diffusivity of deuterium through high-purity beryllium membranes using the gas-driven permeation technique. A multilayer permeation theory is used to analyse the time-dependent and steady-state deuterium flux measurements, in order to determine the diffusivity of the bulk beryllium and to eliminate the surface oxide effects.

2. Experimental

2.1 The samples

In the present study high purity beryllium disks (22 mm in diameter) were used. The samples, supplied by Degusa, were cut from hot isostatic pressed rods, polished and ultrasonically cleaned. Three different samples were tested which will be referred as follows:

Be(1) – 100 μm thick, extra-grade beryllium (99.8%)

Be(2) – 100 μ m thick, high-grade beryllium (99.0%)

Be(3) – 200 μ m thick, the same material as Be (2).

The chemical compositions to the two types of beryllium used are given in Table 2. The surfaces of the two different types of beryllium were analyzed using the Rutherford-Backscattering (RBS) technique. The results indicate a beryllium-oxide layer with thickness of 21 \AA (\pm 10%). Auger-electron spectroscopy with sputter depth profiling confirm the similarity of the oxide films for the different samples.

2.2 The permeation apparatus

The gas membrane permeation system is illustrated in Figure 1. The system consists of two vacuum chambers which are separated from each other by the test membrane. The downstream vacuum chamber is pumped with a turbomolecular pump and has a base pressure of $\sim 10^{-9}$ torr. The upstream chamber is pumped, before the introduction of deuterium, with a liquid nitrogen trapped diffusion pump and a base pressure of $\sim 10^{-7}$ torr is achieved.

Deuterium gas is admitted to the upstream chamber through a servo-controlled leak valve and its pressure is monitored by a high-accuracy capacitance manometer. The downstream deuterium partial pressure is measured by a quadrupole mass spectrometer which is equipped with an electron multiplier. The deuterium flux measurements are calibrated using two deuterium calibrated leaks. The linear pumping speed of the turbomolecular pump, when combined with the high sensitivity of the electron multiplier and the multiple ranges calibration procedure, enables accurate deuterium flux measurements over several orders of magnitude.

In order to achieve reliable measurements, a great deal of care in the system design was taken and blank tests with deuterium were conducted to assure that deuterium can reach the downstream chamber only through the test membrane. In addition, the system is leak-checked after each sample installation using helium in the upstream side and a zero signal in the most sensitive range of the mass spectrometer is achieved.

A microcomputer was used to control the system as well as to collect and analyze the data. The rise-time method was chosen since it allows an independent determination of the diffusivity and the solubility of deuterium in beryllium as explained in the next section. In the present study we measured the permeation over temperatures from 620 to 775K and deuterium pressures from 5×10^3 to 1.3×10^4 Pa.

3. Theory

3.1 Single layer permeation

The equilibrium between a diatomic gas D_2 and a monatomic solid solution of the gas atoms is described by Sievert's law,

$$C = S P^{1/2} \quad (1)$$

where C is the concentration of deuterium in the solid, P is the partial pressure of D_2 in the gaseous phase, and S is known as the Sieverts or solubility constant. In a permeation experiment, a solid membrane of uniform thickness ℓ separates two gaseous phases of pressures P_h and P_ℓ in the high and low pressure sides respectively. The experimental conditions used in our measurements are: $P_\ell = 0$, P_h is instantaneously increased from zero to P_h and then maintained constant, and the initial concentration throughout the membrane is zero. For these conditions the one-dimensional, solution of Fick's laws can be expressed as:⁽⁹⁾

$$J = \frac{DS P_h^{1/2}}{\ell} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-Dn^2 \pi^2 t / \ell^2\right) \right] \quad (2)$$

where J is the flux of deuterium atoms at time t and D is the diffusion coefficient of the solid membrane. The total amount of deuterium which has permeated through the membrane per unit area can be written as:

$$Q(t) = \int J dt = \frac{DS P_h^{1/2}}{\ell} \left[t - \frac{\ell^2}{6D} - \frac{2\ell^2}{\pi^2 D} \times \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-Dn^2 \pi^2 t / \ell^2\right) \right] \quad (3)$$

The diffusion coefficient D can be obtained from the so-called time lag, t_ℓ which is the time-intercept of the line defined by $Q(t)$ curve for $t \rightarrow \infty$. Inspection of Equation (3) shows that,

$$t_e = \frac{\ell^2}{6D} \quad (4)$$

At the steady-state conditions (i.e. $t \rightarrow \infty$) equation (2) becomes:

$$J_{\infty} = \frac{DS P_h^{1/2}}{\ell} \quad (5)$$

which is known as Richardson's equation. The product DS is usually referred to as K , the permeation coefficient or permeability of the solid membrane, so we can write equation (5) as follows:

$$J_{\infty} = \frac{K P_h^{1/2}}{\ell} \quad (6)$$

D, S and K are usually found to follow an Arrhenius relationship, i.e. $D = D_0 \exp(-E_D/RT)$, $S = S_0 \exp(-E_S/RT)$ and $K = K_0 \exp(-E_K/RT)$, where D_0 , E_D , S_0 , E_S , K_0 and E_K are constants which characterize the solid.

3.2 Permeation through a multi-layer media

For a laminated membrane comprised of n individual laminae of materials with diffusion and solubility coefficients D_i and S_i respectively and of uniform thickness ℓ_i , Richardson's equation becomes:

$$J_{\infty} = \frac{P_h^{1/2}}{\sum \ell_i / K_i} \quad (7)$$

where $K_i = D_i S_i$. One can define the effective permeability constant for the composite media as;

$$K_{\text{eff}} = \frac{\ell}{\sum \ell_i / K_i} \quad (8)$$

so equation (7) can be written as

$$J_{\infty} = \frac{K_{\text{eff}} P_h^{1/2}}{\ell} \quad (9)$$

For the case when similar oxide layers are on both metal surfaces we can simply express:

$$K_{\text{eff}} = \frac{\ell}{\delta / K_{\text{ox}} + \ell_m / K_m} \quad (10)$$

where K_{ox} and K_m are the permeability constants of the oxide and the metal respectively, δ is the total oxide thickness and ℓ_m is thickness of the metal. Some authors (for example: Le Claire⁽¹⁰⁾) suggested that in this case J is proportional to a higher power of P_h than $\frac{1}{2}$. However, this was generally observed in hydrogen permeation through oxide films only at low pressures ($P_h < 50$ torr).

Following the method suggested by Yang et al. [11] we can also express the effective diffusion coefficient, D_{eff} (sometimes called the apparent diffusion coefficient). Since both the metal media and the oxide layers contribute to the diffusion time, we can define an effective time-lag as:

$$t_{\ell,eff} = t_{\ell,m} + t_{\ell,ox} = \frac{\ell_m^2}{6 D_m} + \frac{\delta^2}{6 D_{ox}} \quad (11)$$

where $t_{\ell,m}$ and $t_{\ell,ox}$ are the contributions of the metal and the oxide layers, respectively, to the effective time-lag and where D_m and D_{ox} are the diffusion coefficients of the metal and the oxide respectively. Comparing the last equation with equation (4) we find,

$$D_{eff} = \frac{\ell^2}{6t_{\ell,eff}} = \frac{\ell^2}{\frac{\ell_m^2}{D_m} + \frac{\delta^2}{D_{ox}}} \quad (12)$$

which in the case when $\delta \ll \ell$ becomes,

$$D_{eff} = \frac{1}{\frac{1}{D_m} + \left(\frac{\delta}{\ell}\right)^2 \frac{1}{D_{ox}}} \quad (13)$$

There are many cases in which the oxide film is dominant and in which it controls exclusively the effective time-lag measured, and therefore the effective diffusivity. For this case we obtain:

$$D_{eff} = D_{ox} \left(\frac{\ell}{\delta}\right)^2 \quad (14)$$

3.3 Permeation data analysis

During the permeation experiment we collect the deuterium flux ϕ as a function of time. During analysis the effective diffusion and solubility coefficients, D_{eff} and S_{eff} , are determined by the following steps:

- (a) K_{eff} is determined using equation (9) where $J_x = \phi_w/A$ (A is the membrane area).
- (b) The flux data is integrated, the effective time-lag is defined and D_{eff} is calculated using equation (12).
- (c) S_{eff} is calculated from $K_{\text{eff}}/D_{\text{eff}}$.
- (d) These values of D_{eff} and S_{eff} are used as first approximations in a numerical, least-squares fit to equation (2).

After determining the values for D_{eff} and S_{eff} which give the best fit to the experimental data, the independent metal (i.e. beryllium) diffusion coefficients were extracted. This was done using the beryllium-oxide thickness obtained via the RBS analysis together with known values for the tritium diffusion coefficients in BeO^[12] (corrected for deuterium) to solve equation (13) for each measurement and to get the bulk diffusivity. Finally, an Arrhenius plot of the diffusion coefficients of deuterium in the different grades of beryllium was constructed.

4. Results and discussion

To justify the use of Ricardson's equation in our experimental conditions, we first tested the square-root dependence of J_x on P_h . The tests were conducted with sample Be(2) since it was felt that this was the worst-case sample (a higher oxygen content than Be(1) and a bigger ratio of δ/ℓ than Be(3)). The measurements were made at a constant temperature of 725K over the pressure range of 5×10^3 to 1.3×10^4 Pa. After each run, both chambers were pumped continuously until the deuterium flux in the downstream chamber decreased to the background level. The results shown in Figure 2 as $\log J_x$ versus $\log P_h$ and the fitted line

gives $J_s \propto P^n$ where $n = 0.55$. The small deviation from $n = 1/2$ can be easily treated as either a measurement error or to a very small fraction of deuterium which dissolves in the oxide layer as molecules.

The experimental results for the three samples are summarized in Table 3 which gives the values determined for D_{eff} using the method explained in the previous section. Figure 3 shows the diffusivities of deuterium in the two types of beryllium used as a function of the reciprocal temperature. The values were determined using equation (13). In the case of the high-grade beryllium, the calculated results of samples Be(2) and Be(3) were averaged at each temperature. The error bars indicate an accumulation of inaccuracies resulting from the permeation measurements, the oxide film thickness analysis, the calculations and, in some cases, repeated measurements at the same temperature. A least-squares fit of the values appear in this figure yields $D = 6.7 \times 10^{-9} \exp(-28.4/RT)$ [m²/s] for the extra-grade beryllium; and $D = 8.0 \times 10^{-9} \exp(-35.1/RT)$ [m²/s] for the high-grade beryllium samples. Only the higher temperature measurements ($T \geq 700\text{K}$) were used to obtain the values shown in Figure 3, since in the lower temperature range the oxide film is dominant in the determination of D_{eff} . In fact, these lower temperature measurements can serve as independent estimations of the oxide film diffusivity using equation (14) with the RBS results, and they are in good agreement with the values which are reported in Ref. [12].

For comparison, we also draw in Figure 3 the Arrhenius plots given by other authors [3, 4, 8]. Our results tend to agree with the values given by Billone^[8], especially in the case of the extra-grade beryllium .

For both extra-grade and high-grade beryllium we found that the deuterium diffusivity in the bulk, after eliminating the surface effects, is much higher than the values of Jones and Gibson^[4] which are commonly used today for fusion facilities first wall or blanket estimation.

5. Conclusions

- (a) The gas-driven permeation measurements, analyzed using a multilayer permeation theory, have been used to determine the diffusion coefficients of deuterium in extra-grade and high-grade beryllium.
- (b) The Arrhenius equation obtained for the extra-grade beryllium samples is:

$$D = 6.7 \times 10^{-9} \exp\left(-\frac{28.4}{RT}\right) \quad [\text{m}^2/\text{s}]$$

and for the high-grade beryllium is:

$$D = 8.0 \times 10^{-9} \exp\left(-\frac{35.1}{RT}\right) \quad [\text{m}^2/\text{s}]$$

- (c) The diffusivity of deuterium in the two types of high-purity beryllium which were studied by us is much higher than the values which are commonly in use today.
- (d) The inconsistency in the diffusivity of hydrogen isotopes in beryllium might result from variation in sample parameters such as impurities (especially oxygen), preparation processes, and surface condition. For this reason, a reliable estimation of beryllium behaviour in specific fusion reactor design requires testing of samples identical to the actual proposed material.

Acknowledgements

We would like to thank Mr. R. Macaulay-Newcombe for the RBS analysis. We would also like to express our gratitude to the Canadian Fusion Fuels Technology Project (CFFTP) and the Natural Sciences and Engineering Research Council for support of this project.

REFERENCES

- [1] R.W. Moir, Beryllium Usage in Fusion Blankets and Beryllium Data Needs. LLNL Report, UCRL-97426 (1988).
- [2] K.J. Dietz, *J. Nucl. Mater.* 155-157 (1988) 8.
- [3] J.P. Pemsler and E.J. Rapperport, *Trans. Metall. Soc. AIME*, 230 (1964) 90.
- [4] P.M.S. Jones and R. Gibson, *J. Nucl. Mater.* 21 (1967) 353.
- [5] R.M. Al'tovskiy, A.A. Eremin, L.F. Eremina, L.A. Izhevyanov, V.N. Fadeyew and M.I. Urazbayew, *Russ. Metall.* 3 (1981) 51.
- [6] E. Fromm and H. Jehn, *Bulletin of Alloy Phase Diagrams* 5 (1984) 324.
- [7] W.A. Swansiger, *J. Vac. Sci. Technol. A* 4 (1986) 1216.
- [8] M.C. Billone, Private communication (1988).
- [9] J. Crank, *The Mathematics of Diffusion*, 2nd Edition (Oxford University Press, London, 1979).
- [10] A.D. Le Claire, *Diffusion and Defect Data* 33 (1983) 1.
- [11] K. Yang, X.P. Xian, M.Z. Cau, and X.J. Wan, *Scr. Met.* 22 (1988) 355.
- [12] J.D. Fowler, D. Chandra, T.S. Elleman, A.W. Payne, and K. Verghese, *J. Amer. Ceram. Soc.* 60 (1977) 155.

Table 1

Summary of published data on diffusion, solubility and permeation of hydrogen isotopes in beryllium

Authors	Ref. No.		Diffusion Coefficients		Solubility Coefficients		Permeation Coefficients		Temp. range [°K]
			D_0 [m ² /s]	E_D [KJ/mol]	S_0 [mol/m ³ ·√Pa]	E_S [KJ/mol]	K_0 [mol/m·s·√Pa]	E_K [KJ/mol]	
Pemslers and Rapperport	[3]	H	3×10^{-13}	0	-	-	-	-	1123-1173
Jones and Gibson	[4]	T	3×10^{-11}	18.47	1.964×10^{-3}	-1.82×10^{-3}	5.795×10^{-14}	18.47	673-1173
Al'tovskiy et al*	[5]	H	-	-	-	-	4.24×10^{-7}	86.96	773-873
		H	-	-	-	-	3.39×10^{-11}	26.70	773-923
Frømm and Jehn	[6]	H	-	-	2.24×10^{-3}	-1.818	-	-	523-1123
Swansiger	[7]	T	-	-	7.484×10^{-4}	112.8	-	-	713-783
Billone**	[8]	T	1.73×10^{-9}	18.47	-	-	-	-	573-0873
		T	1.35×10^{-10}	0	-	-	-	-	>873

* Two different types of beryllium were studied.

** This reference describes a modified analysis to the experimental data of Jones and Gibson (Ref. 4).

Table 2

The chemical composition in wt% of the beryllium samples as specified by the manufacturer†

	Special grade Be(2) + Be(3)	Extra grade Be(1)
Be min.	99.0	99.8
BeO max.	0.8	0.03
Fe max.	0.07	0.03
Al max.	0.05	0.01
C. max.	0.07	0.03
Si max.	0.04	0.01
Mg max.	0.05	0.006
others max.	0.04	-

† The RBS measurements indicate higher content of oxygen and iron than specified.

Table 3

The effective diffusivity (D_{eff}) [m^2/s] determined from the experimental data

Sample	620°K	660°K	700°K	725°K	750°K	775°K
Be(1)	3.3×10^{-14}	3.4×10^{-13}	2.95×10^{-12}	9.3×10^{-12}	2.3×10^{-11}	5.0×10^{-11}
Be(2)	2.9×10^{-14}	3.7×10^{-13}	2.7×10^{-12}	7.3×10^{-12}	1.6×10^{-11}	2.6×10^{-11}
Be(3)	1.3×10^{-13}	1.4×10^{-12}	7.7×10^{-12}	1.5×10^{-11}	2.5×10^{-11}	3.2×10^{-11}

Figure Captions

- Fig. 1 A schematic drawing of the gas-permeation system.
- Fig. 2 The steady-state deuterium flux (J_{∞}) versus the upstream deuterium pressure (P_H). the fitted line gives: $J_{\infty} \propto P_H^{0.55}$.
- Fig. 3 Arrhenius plots of the diffusivity of deuterium in two different grades of high-purity beryllium. Literature values [3, 4, 8] (corrected for deuterium) are shown for comparison.





