



ELSEVIER

Journal of Nuclear Materials 248 (1997) 159–164

Journal of
nuclear
materials

Tritium recovery from Li17–Pb83 liquid breeder by permeation window method

T. Terai *, A. Suzuki, S. Tanaka

Department of Quantum Engineering and Systems Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract

The tritium permeation window method was demonstrated by out-pile deuterium permeation experiments. The deuterium permeation rate was measured at changing parameters such as the chemical composition of purge gas, the fluidity of Li17–Pb83, the temperature and the condition of surface oxide film to clarify the rate-determining process. The overall mass-transfer coefficient of deuterium from Li17–Pb83 to purge gas through the Nb wall was smaller by 2–5 orders in magnitude than that determined by deuterium diffusion in Nb. This is not due to deuterium diffusion in Li17–Pb83 liquid film but due to the formation of niobium oxides on the surface as a permeation barrier. The permeation rate severely decreased with the growth of surface oxide film and it became too small for an actual blanket system. Therefore, it is necessary to protect the Nb surface from oxidation or to use nobler metals instead of Nb. © 1997 Elsevier Science B.V.

1. Introduction

The lithium lead eutectic alloy (Li17–Pb83 hereafter) is a prominent candidate material for tritium breeding in a CTR liquid blanket because of its high tritium breeding ratio, its low reactivity and possible use as coolant [1]. In addition, Li17–Pb83 has such low tritium solubility that it is much easier to recover tritium from Li17–Pb83 than from liquid lithium. However, the low tritium solubility in Li17–Pb83 results in high partial pressure of tritium, which causes tritium leakage by permeation through a structural metal wall. Thus, continuous and effective tritium recovery is necessary as well as the formation of the tritium permeation barrier by several techniques. From this point of view, several methods, such as gas-bubbling by helium, vacuum degassing in a spray tower, multistage counter current with helium and tritium permeation window, are proposed for tritium recovery from Li17–Pb83.

The tritium permeation window method utilizes the high tritium permeability and the high compatibility of Nb with Li17–Pb83, to recover tritium from Li17–Pb83. This

method had been proposed for tritium recovery from liquid Li. It has, subsequently, been abandoned because a non-metallic film formed on the Nb surface which severely decreases the tritium permeation rate so that a very wide area would be required for the tritium permeation window [2]. On the other hand, it can be a promising method for the recovery of tritium from Li17–Pb83 because the tritium permeation rate is expected to be much larger than it is in the case of Li due to much larger tritium partial pressure over Li17–Pb83.

This paper describes the recovery of hydrogen isotopes from Li17–Pb83 demonstrated by the tritium permeation window method using Nb in out-pile experiments. In particular, the deuterium permeation rate was measured at changing parameters such as the chemical composition of purge gas, the fluidity of Li17–Pb83, the temperature and the condition of the surface oxide film to clarify the rate-determining process, which is a very important factor to design the permeation window system.

2. Experiment

The deuterium permeation experiments were performed in the system shown in Fig. 1. This system consists of a D₂ gas supply system shown as the primary line, a purge gas

* Corresponding author. Tel.: +81-3 3812 2111; fax: +81-3 5800 6824; e-mail: tera@g.t.u-tokyo.ac.jp.

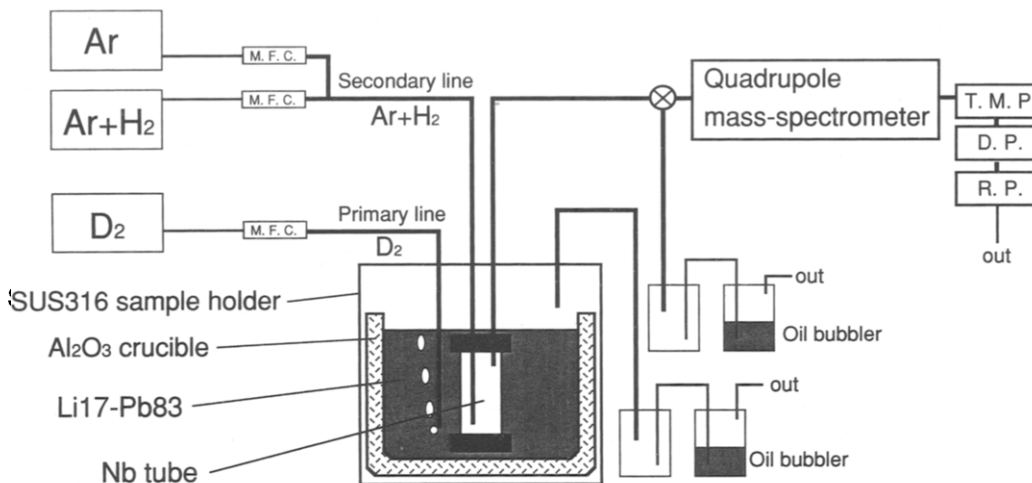


Fig. 1. Apparatus for out-pile experiment.

(Ar + H₂) supply system shown as the secondary line, a Nb tube through which deuterium permeates, a stainless steel type 316 (SUS316) sample holder and a quadrupole mass analyzer system (QMS) monitoring the concentration of deuterium-containing species in the purge gas. The SUS316 sample holder (65 mm in inner diameter, 205 mm in inner depth and 3 mm thick) equipped with a sheathed heater, a thermocouple and a thermal insulator contains an Al₂O₃ crucible (50 mm in inner diameter, 120 mm in inner depth and 5 mm thick) filled with about 1.7 kg of molten Li17–Pb83 and a Nb tube (10 cm long, 7 mm in inner diameter, 8 mm in outer diameter and 99.9% in purity supplied by Nilaco Co.) immersed in the Li17–Pb83 molten alloy. Deuterium, which was dissolved into the Li17–Pb83 alloy by bubbling of D₂ gas in the primary line, permeated through the wall of the Nb tube from the outside to the inside, and the permeating D₂ gas was carried by the purge gas (50–100 cm³/min) in the secondary line to the QMS, with which the partial pressures of deuterium-containing molecules (HD, D₂, HDO and D₂O) were measured. To clarify the rate-determining process similar experiments were also performed without Li17–Pb83 alloy.

The experiments without Li17–Pb83 alloy were carried out using one Nb disk specimen (30 mm in diameter, 0.5 mm thick and 99.9% in purity supplied by Nilaco Co.) and three Nb tube specimens which had different conditions of surface oxide film. The Nb disk specimen (specimen A) was polished to remove the surface oxide film just before the experiment and was kept at 873 K in Ar gas for two days during the experiment. The first Nb tube specimen (specimen B) was kept at 873 K in Ar gas for four days during the experiment. The second Nb tube specimen (specimen C) was kept at 873 K in Ar gas for nine days before the experiment and for another twelve days during the experiment. The last Nb tube specimen (specimen D) was kept at 873 K in Ar gas for thirteen days before the

experiment and for another thirteen days during the experiment. XRD patterns (with Cu–Kα ray) of the rear surfaces of specimen B, C and D after the experiments

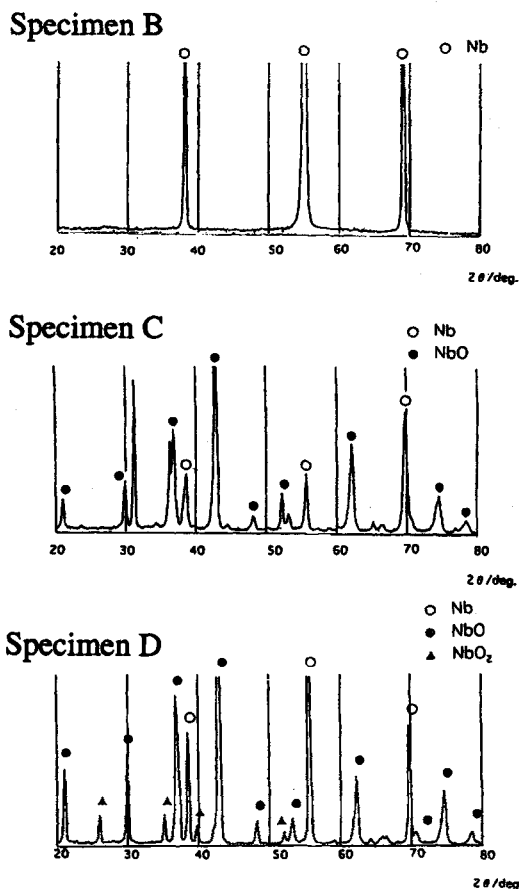


Fig. 2. XRD patterns of the rear surfaces of Nb specimens after permeation experiment (with Cu Kα ray).

without Li17–Pb83 alloy, shown in Fig. 2, indicate that no obvious oxide was observed for the surface of specimen B, while for those of specimens C and D, some niobium oxides such as NbO and NbO₂ were observed. Oxygen diffusion inside the bulk at experimental temperature is considered to be very slow, because the cross section of specimen D remained shiny silver, while the color of both surfaces changed to black NbO and NbO₂ layers. Therefore, it can be said that the polished specimen A had the thinnest surface oxide film and the oxide film grew with time at 873 K. An experiment with Li17–Pb83 alloy was carried out using specimen C after the experiment without the alloy. In this experiment specimen C was kept at 873 K in Ar gas for another six days during the experiment.

Generally, deuterium permeates through a Nb wall through the series of processes shown in Fig. 3. In the experiments without the Li17–Pb83 alloy, deuterium permeates through the following processes: adsorption and absorption of D₂ gas onto the niobium oxide (process 4), deuterium migration in the niobium oxide film on the front surface (process 5), deuterium diffusion in Nb metal (process 6), deuterium migration in the niobium oxide film on the rear surface (process 7) and deuterium desorption from the niobium oxide to the purge gas (process 8). In the experiments with the Li17–Pb83 alloy, on the other hand, the processes through which deuterium permeates are deuterium migration in liquid Li17–Pb83 (process 1), deuterium diffusion in a Li17–Pb83 liquid film covering the Nb surface (process 2), deuterium migration from liquid phase to solid phase (process 3), process 5, process 6, process 7 and process 8. In the present experiments we measured the overall mass-transfer coefficient K , which is

defined as the harmonic mean of the mass-transfer coefficient to each process:

$$\frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2} + \frac{1}{K_3} + \dots \quad (1)$$

To determine the rate-determining process, K was measured under different experimental conditions such as different temperatures (673 K, 773 K and 873 K), different partial pressures of hydrogen in the purge gas (0–7000 Pa), with or without Li17–Pb83 alloy, different fluidity of Li17–Pb83 by changing the flow rate of D₂ gas bubbling, and changing thickness of surface oxide film by oxidation.

The chemical species of permeated deuterium in the purge gas (Ar or Ar + H₂) are HD, D₂, HDO and D₂O, but the moisture species are very difficult to measure because of adsorption to and desorption from the inner wall of the experimental system. Because the signal of the moisture species was always less than 10% of that of molecular hydrogen isotopes, we neglected HDO and D₂O. The deuterium flux for permeation was calculated from partial pressures of HD and D₂ in the purge gas obtained using the calibration curve of QMS.

Deuterium flux J is expressed by the equation

$$J \text{ (mol D/m}^2 \text{ s)} = K' \text{ (mol D/m}^2 \text{ s Pa}^{1/2}) \times [P_{D_2,1}^{1/2} \text{ (Pa}^{1/2}) - P_{D_2,2}^{1/2} \text{ (Pa}^{1/2})], \quad (2)$$

where J is the deuterium flux, K' the mass-transfer coefficient on the basis of D₂ pressure, $P_{D_2,1}$ the D₂ pressure in the primary line and $P_{D_2,2}$ the D₂ pressure in the secondary line. Since $P_{D_2,2} \sim 0$, the mass-transfer co-

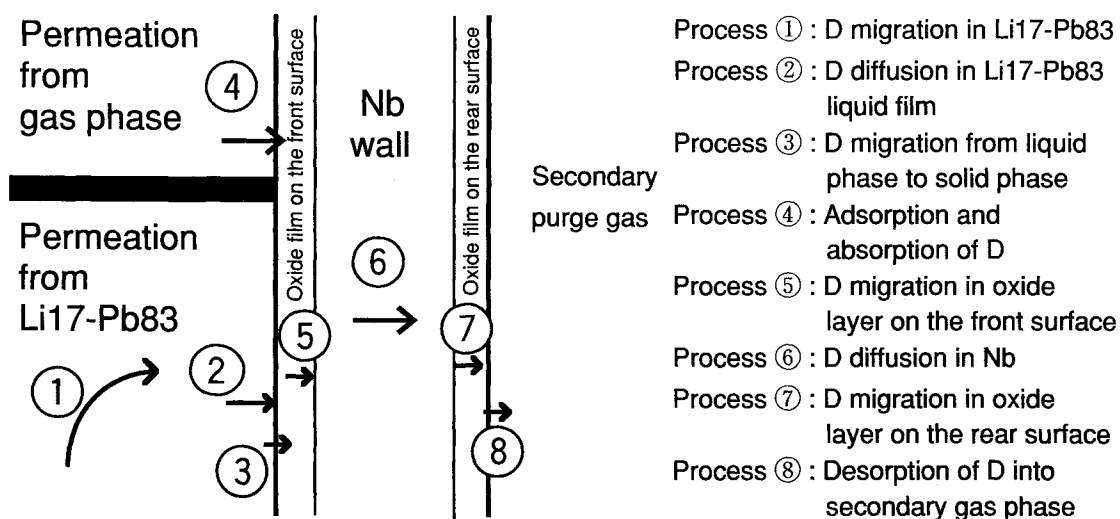


Fig. 3. Deuterium permeation mechanism.

efficient on the basis of deuterium concentration in Li17–Pb83 calculated from K' by the equation

$$K \text{ (m/s)} = \frac{K' \text{ (mol D/m s Pa}^{1/2}) W \text{ (g/mol LiPb)}}{\rho_{\text{LiPb}} \text{ (g/m}^3) K_{s,\text{LiPb}} \text{ (mol D/mol LiPb Pa}^{1/2})} = [J \text{ (mol D/m}^2 \text{ s)} W \text{ (g/mol LiPb)}] / [\rho_{\text{LiPb}} \text{ (g/m}^3) K_{s,\text{LiPb}} \text{ (mol D/mol LiPb Pa}^{1/2}) \times P_{\text{D}_2,1}^{1/2} \text{ (Pa}^{1/2})}] \quad (3)$$

where K is the mass-transfer coefficient on the basis of deuterium concentration in Li17–Pb83, W the average molecular weight of $\text{Li}_{0.17}\text{Pb}_{0.83}$, ρ_{LiPb} the density of Li17–Pb83 and $K_{s,\text{LiPb}}$ the Sieverts constant of deuterium for Li17–Pb83 [3]. In the present experiments, regardless of the presence of Li17–Pb83 alloy, the overall mass-transfer coefficient was evaluated on the basis of deuterium concentration in Li17–Pb83, assuming that the deuterium dissolution rate into molten Li17–Pb83 alloy is very fast.

3. Results and discussion

3.1. Rate-determining process for permeation

In the deuterium permeation experiment without Li17–Pb83 alloy, the following features can be seen on the overall mass-transfer coefficient K from Fig. 4: (1) The overall mass-transfer coefficient K was smaller by 2–5 order of magnitude than that determined by the process of deuterium diffusion in Nb [4], depending on the surface condition of the specimens, and (2) K hardly depended on the partial pressure of hydrogen in the purge gas although the dominant chemical species changed from D_2 to HD

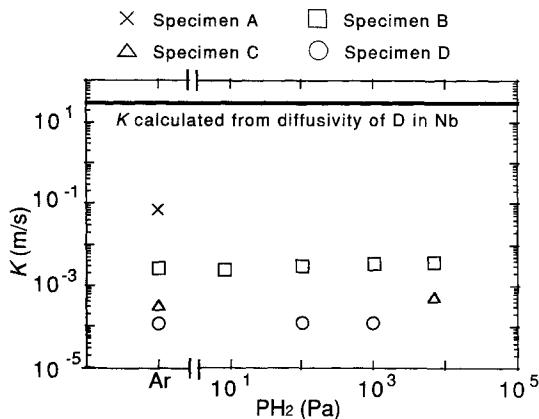


Fig. 4. Dependence of overall mass-transfer coefficient on partial pressure of hydrogen in secondary purge gas for specimen A, B, C and D (in experiments without Li17–Pb83).

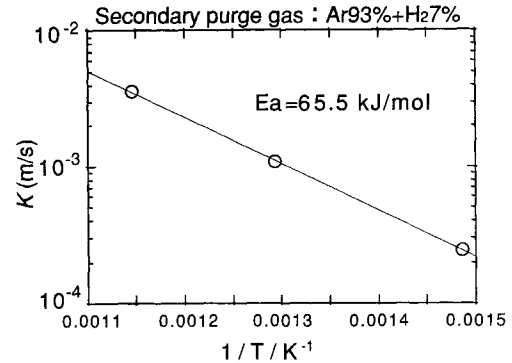


Fig. 5. Temperature dependence of overall mass-transfer coefficients for specimen B.

with increasing H_2 concentration in the purge gas. From the former, it can be said that deuterium diffusion in Nb (process 6) is not the rate-determining process. On the other hand, the latter suggests that deuterium desorption into the purge gas (process 8) is not the rate-determining process, because process 8 is considered to be strongly influenced by H_2 concentration in the purge gas through isotopic exchange reactions. The values of K were different from each other by 2–3 orders of magnitude depending on the condition of surface oxide film; the specimen having a thinner surface oxide film showed a larger value of K . This suggests that the rate-determining process is the deuterium migration in the oxide film on the front and/or the rear surfaces (process 5 and process 7). Activation energy of the mass-transfer coefficient (65.5 kJ/mol) obtained from the temperature dependence of K , shown in Fig. 5, was much larger than the sum of activation energies of deuterium diffusion and dissolution in Nb [5]. This also gives the conclusion that deuterium diffusion in Nb (process 6) is not the rate-determining process. Thus, at the present stage, we can deny the possibility that processes 6 and 8 are rate-determining. Among the remaining processes, deuterium migration in the oxide films (processes 5 and 7) are plausible as the rate-determining process, because deuterium adsorption and absorption (process 4) are considered to be faster than process 8 due to no effect of gas–film resistance.

It is also considered that in the experiment with the Li17–Pb83 alloy the deuterium diffusion in liquid Li17–Pb83 and in a liquid film (processes 1 and 2) are not the rate-determining processes, because no significant effect of the presence of Li17–Pb83 was observed (as shown in Fig. 6). K did not depend on gas flow rate of 0–200 cm^3/min in the primary line with bubbling. This result also shows that neither deuterium migration in liquid Li17–Pb83 (process 1) nor diffusion in a Li17–Pb83 liquid film (process 2) is the rate-determining process. From the value of the diffusion coefficient of deuterium in molten Li17–Pb83 alloy [6], the thickness of the Li17–Pb83 liquid film is

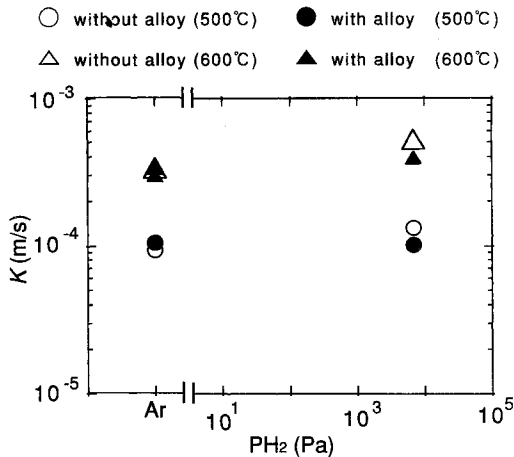


Fig. 6. Effect of the presence of Li17–Pb83 on overall mass-transfer coefficient.

calculated to be much less than 0.01 mm. Regarding process 3, probably, it cannot be the rate-determining process because it is considered to be faster than processes 1 and 2.

To increase the thickness of the rear oxide film, the rear surface was exposed at 873 K to oxygen of 6000 Pa mixed in the purge gas. As a result, K decreased with exposure time, as shown in Fig. 7. This indicates that deuterium migration in the oxide film on the rear surface (process 7) is the rate-determining process. However, it can be said that deuterium migration in the oxide film on the front surface (process 5) may also be the rate-determining process because niobium oxide is more stable thermodynamically than lithium oxide in Li17–Pb83. Therefore, it is concluded that deuterium migration in the surface oxide film (process 5 and process 7) played an important role to determine the deuterium permeation rate through the Nb wall in the experiments with and without Li17–Pb83 alloy.

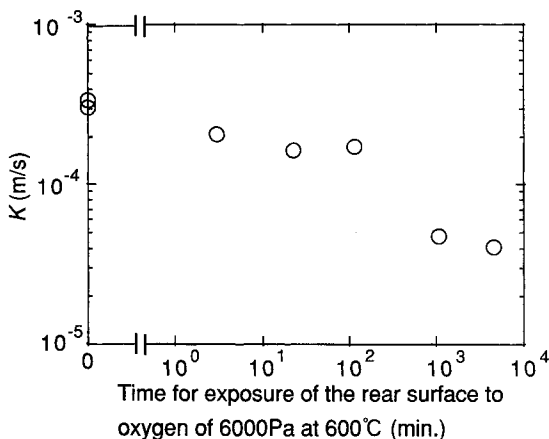


Fig. 7. Effect of the growth of oxide film on the rear surface on overall mass-transfer coefficient.

The value of K was decreased by the growth of the surface oxide film consisting of mostly NbO. It is difficult to increase the overall mass-transfer coefficient to the level determined by the process of deuterium diffusion in Nb from 673 K to 873 K, because Nb tends to be oxidized at the elevated temperatures.

3.2. Evaluation of Nb as a permeation window material

In an actual D–T blanket, it is considered that about 500 g/day of tritium should be recovered and tritium release rate to environment should be less than 10 Ci/day. When we choose a CDC-coating on SUS316 wall ($K \leq 1.0 \times 10^{-7}$ m/s at 873 K) [7] as a tritium permeation barrier and a Nb wall having the same surface condition with specimen C ($K = 4.0 \times 10^{-4}$ m/s at 873 K) as a tritium permeation window, the area of the Nb wall must be 120 times as large as that of the CDC-coated SUS316 wall. With this value, it is difficult to design the blanket system even if the temperature is kept low in the CDC-coated SUS316 area or another tritium barrier is jointly used with the CDC-coated SUS316. If we can use the value calculated from the deuterium diffusibility in Nb having no oxide film, we can make the area of Nb wall 500 times smaller as that of the CDC-coated SUS316. From this point of view, protection of Nb surface from oxidation by noble metal coating is required. Another method for removing surface oxide film is to use nobler metals than Nb as a permeation window material. For example, Fe is 100 times smaller in hydrogen permeability than Nb, but it is four times larger than specimen A in this experiment and 750 times larger than specimen C. In addition, it is known that the Fe surface can be free from non-metallic film acting as a permeation barrier under high hydrogen partial pressure [8] and Fe shows no hydrogen embrittlement like Nb which is an disadvantage of Nb. From these points, Fe is also considered to be a promising material for the tritium permeation window for Li17–Pb83.

4. Conclusion

The rate-determining process for deuterium permeation through an Nb wall is deuterium migration in the surface oxide film and the permeation rate was sensitively decreased by the growth of the surface oxide film consisting of mostly NbO. The permeation rate through the Nb specimen observed in this experiment was so small for the application to an actual blanket system that it is necessary to protect the surface from oxidation or to use nobler metals which can be free from non-metallic films.

References

- [1] S. Malang, P. Leloy, G.P. Casini, R.F. Mattas, Y. Strebkov, Fusion Eng. Des. 16 (1991) 95.

- [2] S. Tanaka, H. Katsuka, K. Furukawa, R. Kiyose, *J. Nucl. Mater.* 97 (1981) 59.
- [3] D.W. Rudd et al., *J. Chem. Phys.* 66 (1962) 351.
- [4] A.S. Nowick, J.J. Burton, eds., *Diffusion in Solids* (Academic Press, New York, 1975) p. 232.
- [5] G. Alefeld, J. Voelkl, eds., *Hydrogen in Metals 1* (Springer, Berlin, 1978) p. 330.
- [6] T. Terai, S. Nagai, T. Yoneoka, Y. Takahashi, *J. Nucl. Mater.* 187 (1992) 247.
- [7] T. Terai, T. Yoneoka, H. Tanaka, H. Kawamura, *J. Nucl. Mater.* 212–215 (1994) 976.
- [8] T. Terai, K. Uozumi, Y. Takahashi, *Proc. SOFT-17*, 1993, p. 1518.