ELSEVIER

Journal of Nuclear Materials 248 (1997) 106–110

journal of nuclear materials

Isotope exchange capacity of solid breeder materials

Atsushi Baba [a,*], Masabumi Nishikawa [a], Yoshinori Kawamura [b], Kenji Okuno [b]

[a] *Department of Nuclear Engineering, Faculty of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-81, Japan*
[b] *Tritium Engineering Laboratory, Japan Atomic Energy Research Institute, Shirakata Shirane 2-4, Tokai-mura, Naka-gun, Ibaraki-ken 319-11 Japan*

Abstract

Though lithium ceramic materials such as Li_2O, $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 are considered as the candidates of tritium breeding materials in the blanket of a D–T fusion reactor, the release behavior of the bred tritium in these solid breeder materials is not yet fully understood. It is observed in this study that $LiAlO_2$ or Li_4SiO_4 has an additional capacity for tritium uptake on the surface through isotope exchange reactions, the isotope exchange capacity, other than the adsorption capacity. It is considered that some -OH bases attributed to the strongly bound chemically adsorbed water or the crystal water formed on the grain surface act as tritium trap, when the isotope exchange reaction are active. It is also observed in this study that Li_2ZrO_3 has no isotope exchange capacity. Effects of the isotope exchange capacity on the tritium inventory in the breeding blanket is discussed based on the data observed in this study where effects of diffusion of tritium in the grain, absorption of water in the bulk of grain and adsorption of water on the surface of grain together with isotope exchange reactions are considered. © 1997 Elsevier Science B.V.

1. Introduction

The release of tritium bred in the solid breeder material consist of the processes of diffusion and bulk absorption in the grain of lithium ceramics, surface reaction on the grain, diffusion through pores of sintered particle and diffusion through the boundary layer formed on the particle surface to the purge gas. Adsorption or desorption and two types of isotope exchange reactions, isotope exchange reaction between H_2 in the purge gas and tritium on the grain surface and that between H_2O in the purge gas and tritium on the grain surface, contribute as the surface reactions. Understanding of the transfer mechanisms by which tritium migration through the breeder material are controlled, the tritium inventory in a blanket or the response behavior of tritium in the purge gas following change of some operating conditions of blanket system is determined if the system effect in the piping of apparatus and the memory effect in the monitor system are properly excluded. Most results of the in situ experiments so far are analyzed assuming that the overall release process is mainly controlled by diffusion in the crystal grain. However, it has been pointed out recently that contribution of the surface reactions can not be ignored [1–4], though the system effect or the memory effect is not cleared. The present authors have quantified the amount of water captured in Li_2O, $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 in the previous papers [5–8] and have compared the tritium inventory at the blanket due to sorption with that due to diffusion in the crystal grain, and have pointed out that inventory due to sorption is much larger than that due to diffusion unless otherwise a large amount of H_2 or water vapor is swamped to the purge gas in the high temperature blanket.

Some -OH bases attributed to the strongly bound chemically adsorbed water or crystal water formed on the grain surface of a solid breeder material at the pellet manufacturing process can act as tritium trap through isotope exchange reactions.

The isotope exchange capacity for $LiAlO_2$ is experimentally obtained in this study, and then discussions on tritium inventory in the $LiAlO_2$ blanket under the steady state condition are performed in this study considering diffusion, absorption, adsorption and isotope exchange reactions.

---

[*] Corresponding author. Tel.: +81-92 642 3785; fax: +81-92 642 3784; e-mail: ababatne@mbox.nc.kyushu-u.ac.jp.

0022-3115/97/$17.00
PII S0022-3115(97)00167-0

2. Inventory estimation method

Contribution of tritium diffusion in the crystal grain, absorption of water into bulk of lithium ceramic, adsorption of water onto the grain surface, isotope exchange reaction between H_2 in the purge gas and tritium on the grain surface and isotope exchange reaction between H_2O in the purge gas and tritium on the grain surface are considered in estimation of the tritium inventory under the steady state condition as follows.

In our experiments on $LiAlO_2$, occurrences of absorption of HT or HTO and adsorption of HT have not been observed yet. Accordingly, absorption inventory is excluded in consideration of this study.

The diffusion inventory in the blanket packed with solid breeder particles made of spherical grain is given as

$$I_D = G_T d_p^2 / 60 D_T \text{ (mol T)}, \tag{1}$$

where G_T [mol/s] is the tritium generation rate in the blanket, d_p [m] is the grain diameter and D_T [m^2/s] is the diffusivity of tritium in grain.

Then, the average residence time due to diffusion is given by I_D/G_T.

The adsorption inventory is given by the following equation when contribution to the T/H ratio on the grain surface from the both isotope exchange reactions can be supposed to be same:

$$I_{ad} = Q_{ad} M P_{T_2O} / \left(P_{H_2} + P_{T_2O} + P_{H_2O} + P'_{H_2O} \right) \text{ (mol T)}, \tag{2}$$

where P_{H_2} [Pa] is the partial pressure of H_2 in the purge gas, P_{H_2O} [Pa] is the partial pressure of H_2O swamped to the purge gas, P'_{H_2O} [Pa] is the partial pressure of residual H_2O in the purge gas, and M [mol] is amount of Li ceramics in blanket.

The partial pressure of tritium in the purge gas, P_{T_2O}, is given as

$$P_{T_2O} = P_{He} G_T / G_{He} \text{ (Pa)}, \tag{3}$$

where all tritium bred in the grain is considered to be released in the chemical form of water and P_{He} [Pa] and G_{He} [mol/s] are the total pressures of helium purge gas and flow rate, respectively.

The amount of water adsorption, Q_{ad}, is given as

$$Q_{ad} = C_{ad} A_{BET} P^n \exp(-E_{ad}/RT) \text{ (mol/mol)} \tag{4}$$

in the previous papers [5–8], where A_{BET} is the BET surface area of the breeder particle and E_{ab} is the heat of absorption. The total partial pressure of water in various form is given as

$$P = P_{T_2O} + P_{H_2O} + P'_{H_2O} \text{ (Pa)}. \tag{5}$$

Then, the average residence time due to adsorption is given by I_{ad}/G_T.

The tritium inventory due to isotope exchange capacity is given as

$$I_{ex} = Q_{ex} M P_{T_2O} / \left(P_{H_2} + P_{T_2O} + P_{H_2O} + P'_{H_2O} \right) \text{ (mol T)}, \tag{6}$$

where Q_{ex} [mol/mol] is the isotope exchange capacity on the grain surface other than adsorbed water and is probably due to –OH base strongly bound to the grain surface.

The average residence time due to isotope exchange capacity is given by I_{ex}/G_T.

Then, the total inventory in the blanket is given as

$$I_{Tot} = I_D + I_{ad} + I_{ex} \text{ (mol T)}. \tag{7}$$

In estimation of I_{ad}, the values for n, C_{ad} and E_{ad} are taken from our previous work [6] as 1/2, 2.6×10^{-7} mol g/mol m^2 $Pa^{1/2}$ and 32.2 kJ/mol, respectively.

3. Experimental

The same experimental apparatus and the same experimental procedure are employed to measure the tritium behavior in the packed bed of lithium ceramics as those descried in the previous papers [9,10]. The same $LiAlO_2$, Li_2ZrO_3 or Li_4SiO_4 particles as those used in the experiments to study the adsorption characteristics of water are also used in this study.

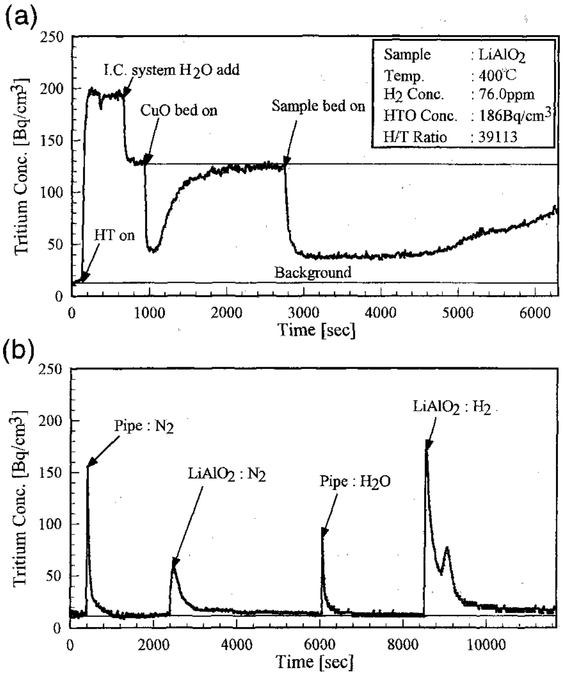


Fig. 1. (a) The example of output curve of the ionization chamber (sorption step). (b) The example of output curve of the ionization chamber (desorption step).

Fig. 1a shows the change of reading of an ionization chamber with time after introduction of HTO/N_2 gas to the system where HTO is formed by oxidation of HT applying the hot CuO bed. The first decrease of reading obtained when the channel to the $LiAlO_2$ packed bed in the quartz tube is closed corresponds to tritium sorption onto the surface of piping and casing of the ionization chamber through adsorption and isotope exchange reaction. The second decrease obtained when the channel to the packed bed is connected corresponds to tritium sorption to $LiAlO_2$, quartz tube and piping around the packed bed.

Fig. 1b shows the reading obtained when desorption operation is performed using dry N_2, humidified N_2 or H_2/N_2 as the purge gas after sorption operation as shown in Fig. 1a. The second and fourth peaks correspond to tritium from $LiAlO_2$, quartz tube and piping around the packet bed.

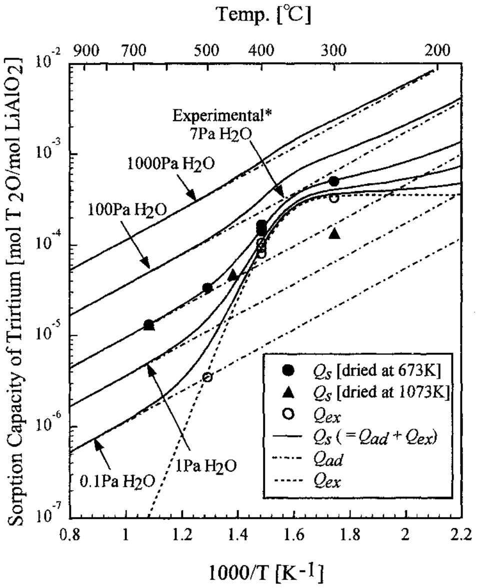
The amount of tritium captured to $LiAlO_2$ itself is obtained by subtraction of tritium sorbed to quartz tube and piping evaluated from the blank test from the amount of tritium evaluated from the second concavity at sorption experiment as shown in Fig. 1a or from the second and fourth peaks in desorption experiment as shown in Fig. 1b. Further subtraction of the adsorption capacity estimated using the correlative equation reported elsewhere by the present authors from the amount of tritium captured to $LiAlO_2$ gives the isotope exchange capacity.

4. Results and discussion

4.1. Isotope exchange capacity

The isotope exchange capacities obtained for $LiAlO_2$ previously dried under N_2 gas stream at 673 K for 6 h are shown in Fig. 2 and the following equation is obtained. The obtained values at 873 K can be regarded to be zero in the range of experimental precision:

$$Q_{ex} = \frac{2.7 \times 10^{-15} A_{BET} \exp(144\ \mathrm{kJ}/RT)}{1 + 2.2 \times 10^{-12} \exp(144\ \mathrm{kJ}/RT)}\ (\mathrm{mol/mol}). \tag{8}$$



* Converted to 7Pa

Fig. 2. The isotope exchange capacity for $LiAlO_2$.

The similar tendency of isotope exchange capacity with temperature has been obtained by the present authors also for Pt-activated alumina catalyst [11].

It can be said from above observation that the isotope exchange capacity may consist a major part of the tritium inventory of the $LiAlO_2$ blanket when temperature is lower than 773 K.

It is also observed in this study that no isotope exchange capacity is found even at 573 K when 1073 K is applied for temperature in the previous drying. Accordingly, sorbed amount of tritium to the $LiAlO_2$ sample previously dried at 1073 K agrees with the adsorption capacity in the whole temperature range as also shown in Fig. 2. Observation that no distinguishable difference was seen in the SEM pictures taken before and after heating implies that disappearance of the isotope exchange capacity can not be attributed to the change of external appearance.

Tanaka et al. have observed using FTIR that the signal corresponding to a certain –OH base disappears from the

Table 1
Isotope exchange capacity for $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 at 673 K.

	$LiAlO_2$		Li_2ZrO_3		Li_4SiO_4
Sample weight (g)	5.33	5.33	20	20	20.04
T Conc. (μCi/cm^3)	0.01640	0.00289	0.01470	0.00502	0.04650
H_2 Conc. (ppm)	64.5	80.0	70.8	81.8	32.5
H/T Ratio (–)	10200	71500	12500	39900	1800
T Captured (mol/mol)	1.41×10^{-4}	1.61×10^{-4}	7.69×10^{-6}	7.76×10^{-6}	5.49×10^{-5}
T Adsorbed (mol/mol)	6.09×10^{-5}	6.78×10^{-5}	10.1×10^{-6}	10.8×10^{-6}	1.91×10^{-6}
T Exchanged (mol/mol)	8.00×10^{-5}	9.30×10^{-5}	–	–	5.17×10^{-5}

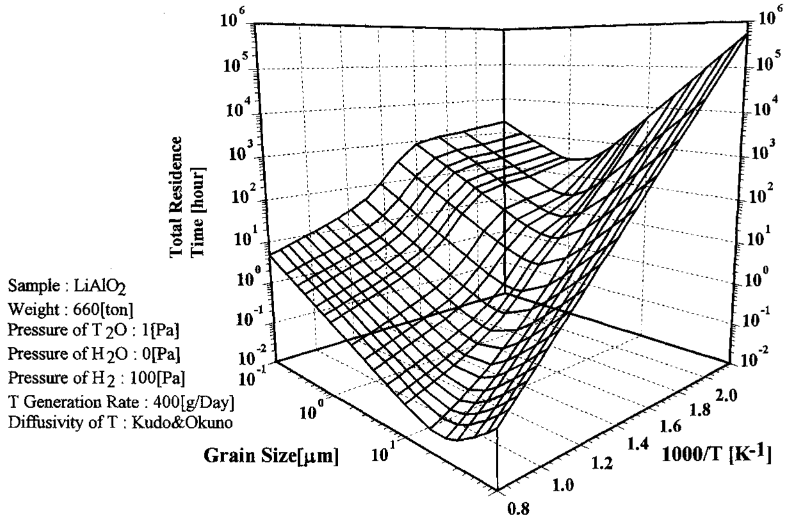


Fig. 3. Estimated values of the total residence time for $LiAlO_2$ blanket (P_{T_2O}: 1 Pa; P_{H_2O}: 0 Pa; P_{H_2}: 100 Pa; M: 660 ton, G_T: 400 g/day; D_T: Kudo and Okuno).

Li_2O surface when it is heated to 973 K and that recovery of that –OH base is not recognized even when temperature is lowered in the humidified atmosphere [12]. It is considered by the present authors that the similar phenomenon occurs also on the $LiAlO_2$ surface though it is not certified. Then, it is presumed that a certain –OH base or water trapped in the $LiAlO_2$ matrix in the course of the pellet manufacturing process may act as the isotope exchange capacity till they are released at high temperature. Further phenomenological discussion is required to clarify behavior of tritium on the solid breeder materials though only the quantitative analysis is performed in this study. At any rate, observations in this study imply that the previous drying of $LiAlO_2$ above 1073 K can diminish tritium inventory to a large extent even in a low temperature blanket. The isotope exchange capacities observed for $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 are compared in Table 1. It is shown in this table that Li_2ZrO_3 has no isotope exchange capacity though $LiAlO_2$ and Li_4SiO_4 have large exchange capacities.

4.2. Average residence time

Estimated values of the total average residence time for $LiAlO_2$ blanket purged by 100 kPa He with 100 Pa H_2 at various temperature and grain sizes using diffusivity by Kudo and Okuno [13] is shown three dimensionally in Fig. 3 where operating of a 1 GW D–T fusion reactor (overall thermal conversion efficiency: 30%) with $LiAlO_2$ blanket having 70 tons of Li is supposed. Then, total residence time of 1 h corresponds to the tritium inventory of 16.7 g in the whole blanket. Effect of temperature on residence time when grain size is used as parameter is compared in Fig. 4 also for the blanket purged by He with 100 Pa H_2.

It is known from these figures that contribution of diffusion inventory can not be excluded in estimation of the tritium inventory in the $LiAlO_2$ blanket purged by He with 100 Pa H_2 even when the grain size is more than 10 μm.

The region in which more than 90% of the total inventory is occupied by the diffusion inventory is named the diffusion controlling region in this study. Then, there exist diffusion controlling and adsorption controlling regions with a intermediate region in those figures.

As can be seen from Eqs. (1), (2) and (6), effects of

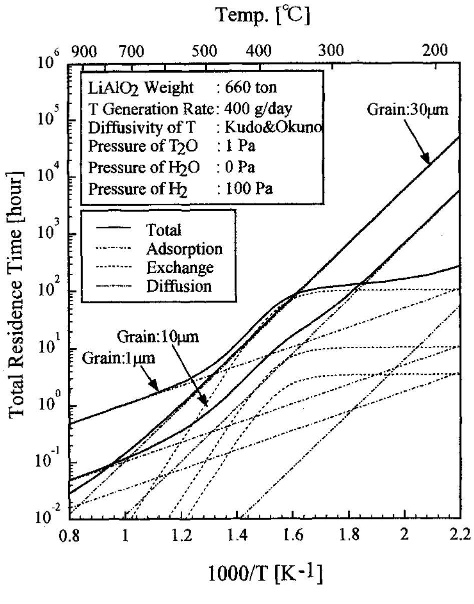


Fig. 4. Effect of temperature on residence time for $LiAlO_2$ blanket (He + 100 Pa H_2 purge; D_T: Kudo and Okuno).

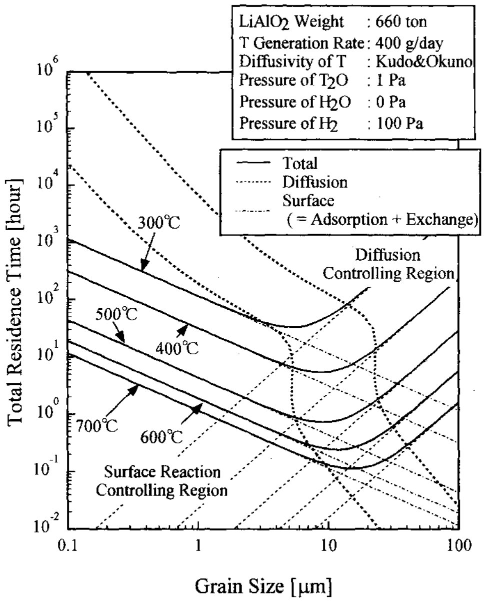


Fig. 5. Effect of grain size on residence time for $LiAlO_2$ blanket (He + 100 Pa H_2 purge; D_T: Kudo and Okuno).

tritium generation rate, temperature, grain size, partial pressure of H_2, partial pressure of water vapor or flow rate of purge gas on tritium inventories are different in each controlling region. Accordingly, it is necessary to understand the situation dominating the tritium behavior in blanket for optimization of bred tritium recovery system.

Contribution of diffusion to the total inventory decreases with increase of temperature and with decrease of grain size as shown in Fig. 5 and it can be ignored at temperature around 200°C if diffusivity by Kudo and Okuno is used. When 100 Pa H_2 is added to the He purge gas, diffusion controlling region extends to the smaller grain size range because of decrease of the surface inventory due to isotope exchange reaction.

5. Conclusions

The tritium inventory in the $LiAlO_2$ blanket under the steady state condition is estimated considering diffusion in grain, adsorption on the grain surface and two isotope exchange reactions between H_2 or H_2O and tritium on the grain surface where isotope exchange capacity is experimentally obtained in this study.

References

[1] T. Kurasawa, H. Watanabe, G.W. Hollenberg, J. Nucl. Mater. 155–157 (1988) 544.
[2] H. Werle et al., J. Nucl. Mater. 155–157 (1988) 538.
[3] J.P. Kopasz, S.W. Tam, C.E. Johnson, J. Nucl. Mater. 155–157 (1988) 500.
[4] G. Federici, A.R. Raffray, M.A. Abdou, J. Nucl. Mater. 173 (1990) 185.
[5] K. Munakata, M. Nishikawa, K. Yoneda, Fusion Technol. 15 (1989) 1451.
[6] Y. Kawamura et al., J. Nucl. Sci. Technol. 29 (1992) 436.
[7] Y. Kawamura, M. Nishikawa, K. Tanaka, J. Nucl. Mater. 208 (1994) 308.
[8] Y. Kawamura, M. Nishikawa, J. Nucl. Mater. 218 (1995) 218.
[9] M. Nishikawa et al., Fusion Technol. 21 (1992) 878.
[10] M. Nishikawa et al., Fusion Technol. 28 (1995) 1233.
[11] M. Nishikawa et al., J. Nucl. Sci. Technol. 26 (1989) 261.
[12] M. Taniguchi, H. Watanabe, S. Tanaka, T. Terai, Proc. Ann. Mtg. AESJ., Osaka, Mar. 27–29, M13 (1996).
[13] H. Kudo, K. Okuno, J. Nucl. Mater. 155–157 (1988) 524.