Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Journal of Nuclear Materials 335 (2004) 70–76

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Release behavior of bred tritium from $LiAlO_2$

M. Nishikawa [a,*], T. Kinjyo [a], T. Ishizaka [a], S. Beloglazov [a], T. Takeishi [a], M. Enoeda [b], T. Tanifuji [c]

[a] *Graduate School of Engineering Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan*
[b] *Naka Establishment, Japan Atomic Energy Research Institute, JAERI, Ibaraki 319-1195, Japan*
[c] *Tokai Establishment, Japan Atomic Energy Research Institute, JAERI, Ibaraki 319-1195, Japan*

Received 19 February 2004; accepted 3 July 2004

Abstract

The release behavior of bred tritium to the blanket purge gas is mainly controlled by such bulk phenomena as tritium forming reaction, diffusion of tritium in grain, interaction of tritium with irradiation defects, and absorption together with such surface phenomena as adsorption, isotope exchange reaction between molecular form hydrogen in purge gas and tritium on grain surface (isotope exchange reaction 1), isotope exchange reaction between water vapor and tritium on grain surface (isotope exchange reaction 2), and water formation reaction at addition of hydrogen. Following the observation of the present authors that the isotope exchange reaction 2 is much faster than the isotope exchange reaction 1, the release curve of bred tritium obtained at purge with humidified gas was used for estimation of the effective diffusivity of bred tritium in $LiAlO_2$. Then, the effective diffusivity of tritium in grain of $LiAlO_2$ is obtained as $D_T = 2.5 \times 10^{-7}\exp(-110\ [\mathrm{kJ}]/RT)\ [\mathrm{m^2/s}]$. This equation gives the larger diffusivity than any other diffusivity presented so far because the mass transfer resistance at the grain surface is expected to be eliminated in the estimation procedure of this study.

PACS: 28.52.Fa; 28.52.Lf

1. Introduction

It is required to develop an efficient tritium fueling cycle keeping the over-all tritium breeding ratio greater than 1.0 and a reliable tritium confinement system assuring the radiation safety of tritium in construction of the D–T fusion reactor. The blanket is the place where the tritium recovery system has contact with the cooling system for electricity generation at the elevated temperature. Then, understanding of release behavior of bred tritium is important for design of efficient blanket to recover bred tritium with minimum permeation loss. Tritium release behavior in the breeding blanket is discussed in this paper targeting at the diffusivity of bred tritium in $LiAlO_2$ grain because discrepancy in the reported values for tritium diffusivity in $LiAlO_2$ so far is so large to design a blanket tritium system.

---

[*] Corresponding author. Tel.: +81 92 642 3783; fax: +81 92 642 3800.

E-mail address: nishikaw@nucl.kyushu-u.ac.jp (M. Nishikawa).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.07.032

It seems to be taken as the common recognition to add about 1000 ppm of hydrogen to the blanket purge gas probably for recovery of tritium as HT form, and the recovery method of the bred tritium is discussed so far mostly based on this recognition, though the reason has not been clearly explained. It has been reported by the present authors that water vapor is generated from various solid breeder materials at introduction of hydrogen to the purge gas at the elevated temperature [1–3]. It has been also reported by the present authors that the isotope exchange reaction between tritium on the grain surface of breeder material and water vapor in the purge gas, named as the isotope exchange reaction 2 by the present authors, is much faster than desorption reaction of water from grain surface or isotope exchange reaction between tritium on grain surface and hydrogen in gas phase (named as the isotope exchange reaction 1) [4–6]. Then, use of the tritium release curve obtained at purge using purge gas with hydrogen for estimation of diffusivity may not exclude the effect due to mass transfer resistances on the grain surface.

In this study, change of release behavior of bred tritium from $LiAlO_2$ with change of purge gas composition was compared using the thermal release after irradiation method, where neutron irradiation was performed at Japan Research Reactor-3 (JRR-3) in Japan Atomic Energy Research Institute (JAERI) or the Kyoto University Research Reactor (KUR reactor) in Kyoto University. The effective diffusivity of tritium in $LiAlO_2$ grain was quantified using the release curve obtained at purge using the humidified nitrogen.

2. Preparatory consideration

In order to understand the tritium behavior in a blanket system packed with sintered pebbles of micro crystal grains of ceramic breeder material, it is necessary to know the contribution of such tritium transfer steps as (1) tritium formation reaction in crystal grain, (2) diffusion of tritium in crystal grain to the grain surface, (3) interaction of migrating tritium with irradiation defects formed in crystal grain, (4) absorption of tritium into bulk of crystal grain, (5) adsorption or desorption of tritium on grain surface, (6) isotope exchange reaction between molecular form hydrogen, H_2, in the gas stream and tritium on grain surface (isotope exchange reaction 1), (7) isotope exchange reaction between water vapor, H_2O, in the gas stream and tritium on grain surface (isotope exchange reaction 2), (8) water formation reaction on grain surface at addition of H_2 to the blanket purge gas especially at high temperature, (9) transfer of hydrogen isotopes and water through pores of the sintered pebble, and (10) transfer of hydrogen isotopes and water through boundary layer formed on the surface of a sintered pebbles to the gas stream. The tritium migration model from grain of solid breeder material to the blanket purge gas following the above consideration is conceptually shown in Fig. 1.

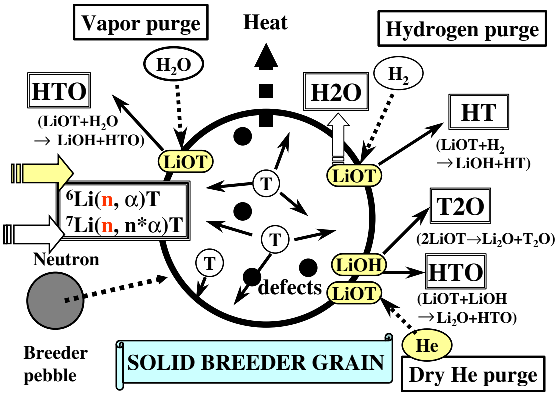

Fig. 1. Conceptual figure of tritium transfer steps from solid breeder material.

Steps (1)–(3) decide the diffusion inventory of tritium which corresponds to the amount of tritium in the bulk of crystal grains when no absorption occurs. These steps also give the effective diffusivity of bred tritium if the mass transfer resistance due to reactions on the grain surface is eliminated from the tritium release curve. Step (5) decides the absorption inventory due to absorption of water vapor or molecular form hydrogen into the bulk of grain. The present authors have observed that water vapor is absorbed into Li_2O at the higher blanket temperature though Li_2TiO_3, $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 have no detectable absorption capacity of water or molecular form hydrogen. Steps (4), (6), (7) and (8) decide the surface inventory of tritium which corresponds to the amount of tritium on the surface of crystal grains. These reactions compete at the grain surface also to decide the chemical form of tritium released into the purge gas. Then, it can be said that the amount of tritium permeable from blanket system to coolant of electricity generation system is controlled by steps (4), (6), (7) and (8). Step (9) decides the tritium inventory in micro pores of the sintered pebbles. Step (10) decides the tritium inventory under diffusion through the boundary layer formed around the sintered pebbles. The experimental observations about the tritium inventory so far indicate that effect of steps (9) and (10) are negligible [4,5].

It must be kept in mind that the same amount of oxygen as bred tritium is also liberated from the breeder materials to make water with hydrogen added to the blanket purge gas.

Above considerations indicate that quantification of the surface phenomena is required to make quantification of the bulk phenomena from the tritium release curve.

3. Experimental

Release curves of bred tritium from $LiAlO_2$ (75.1% of theoretical density, grain size 10 μm, pebble size 4 mm, made by JAERI) were obtained applying the out-pile temperature programmed desorption method using the experimental apparatus of which schematic diagram is shown in Fig. 2. A 0.4–1 g sample of breeder particles contained in a quartz tube filled with helium gas was irradiated with the thermal neutron at JRR-3 reactor in JAERI or at KUR reactor in Kyoto University. The flux of thermal neutron was 4.0×10^{13} and $1.6–2.8 \times 10^{13}$ n/cm^2s in JRR-3 and KUR, respectively, and the irradiation time was varied from 3 to 100 min. The irradiated sample was purged by dry N_2 gas, N_2 gas with hydrogen in various concentrations or N_2 gas with water vapor in various concentrations, and the temperature of the sample bed was changed linearly from room temperature to 1073 K with the rising rate of 2.5, 5 or 10 K/min. The flow rate of the purge gas was 100 STP cm^3/min. The release behavior of total tritium, HT and HTO, was measured using the first 50 cc ionization chamber connected to the experimental apparatus shown in Fig. 2 where humidified N_2 gas was introduced to the purge gas at the inlet of the ionization chamber to diminish the memory effect following the result reported elsewhere [7–9]. The release behavior of tritium as the HT form was followed by the second ionization chamber placed after the water bubbler.

After the purging procedure of each sample was finished, purge of the apparatus using the humidified N_2 gas was performed to estimate the amount of tritium trapped to the surface of piping between outlet of sample bed and inlet of first ionization chamber. This amount of tritium contamination is considered to be negligible at the case where the bred tritium is released to the purge gas in the HT form because the trapping rate of tritium to the piping surface through the isotope exchange reaction 1 is very slow as reported by the present authors [10,11].

4. Results and discussion

Example of the release curves of total tritium and tritium of HT form observed for $LiAlO_2$ at purge by dry N_2 gas, N_2 gas with hydrogen and N_2 gas with water vapor are compared in Figs. 3–5, respectively. It can been seen from comparison of these figures that the fastest tritium release is observed when the purge gas with water vapor is applied and a little slower release is observed when the purge gas with hydrogen is applied and much slower release is obtained in the case of the purge by dry gas, though the purge by hydrogen gives much slower release curve similar to the purge by dry gas at tritium release from Li_4SiO_4, Li_2TiO_3 and Li_2ZrO_3 as reported by the present authors [12,13]. It is mentioned in the previous report by the present authors about the tritium inventory in a $LiAlO_2$ blanket that $LiAlO_2$ has a rather large isotope exchange capacity other than the adsorption capacity on the grain surface [4]. It is supposed in this study that dilution of tritium with hydrogen of the isotope exchange capacity at the grain surface makes the release of bred tritium slower as shown by Fig. 3. It can be seen from Fig. 4 that a majority of the bred tritium is released in the HT form from $LiAlO_2$ at purge with hydrogen though almost all tritium is released in the HTO form from Li_4SiO_4, Li_2TiO_3 and Li_2ZrO_3 as reported in the previous paper where the same experimental procedure was taken as that taken in this study [14].

The reactions considered to occur on the grain surface of solid breeder materials at tritium release are listed in Table 1 for various temperature regions under various purge gas conditions. It is considered by the present authors that the competition of water desorption

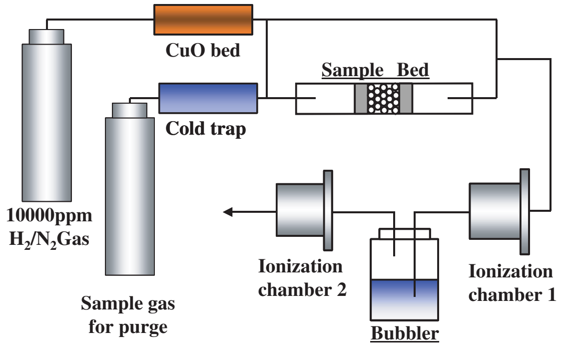

Fig. 2. Schematic diagram of experimental apparatus having two ionization chambers.

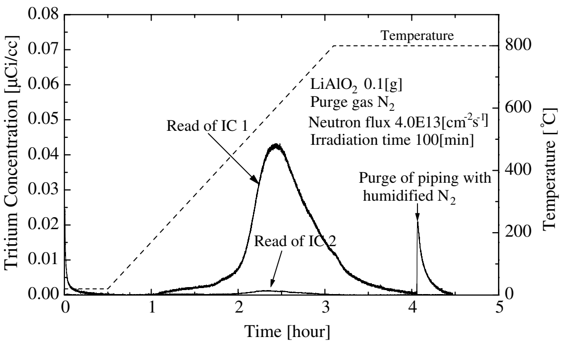

Fig. 3. Tritium release curve from $LiAlO_2$ observed at purge using dry N_2 gas.

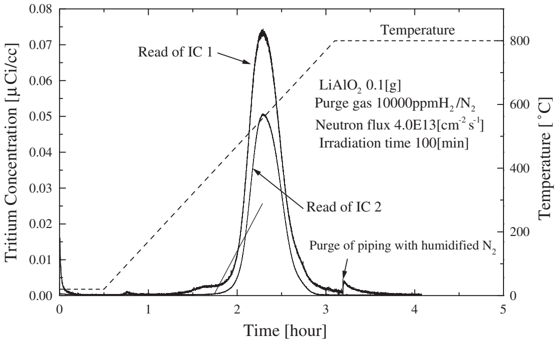

Fig. 4. Tritium release curve from $LiAlO_2$ observed at purge using N_2 with 10000 ppm hydrogen.

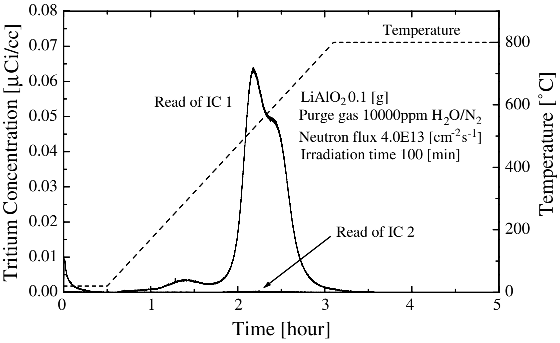

Fig. 5. Tritium release curve from $LiAlO_2$ observed at purge using N_2 with 10000 ppm water vapor.

reaction which releases tritium as HTO, isotope exchange reaction 1 which releases HT and isotope exchange reaction 2 which releases HTO decides the ratio of HTO to HT. Most bred tritium is released in the HTO form at the lower temperature than 600 K even when hydrogen is applied to the purge gas because the isotope exchange reaction 1 is much slower than the desorption reaction or the isotope exchange reaction 2 at the lower temperature range [4,5]. In the case of $LiAlO_2$, however, release of bred tritium begins at high temperature due to small diffusivity. Then, the isotope exchange reaction 1 becomes effective to liberate more tritium in the form of HT as discussed in the previous paper [14].

It is shown in Figs. 3 and 4 that some tritium is quickly liberated soon after switch of the purge gas from N_2 or N_2 with hydrogen to humidified N_2 after the purging procedure of irradiated sample by N_2 or N_2 with hydrogen is finished. Tritium release of this manner is not observed when purge of the irradiated sample is performed using the humidified purge gas as shown in Fig. 5. Accordingly, it is considered by the present authors that the tritium trapped to the piping surface between sample bed and the first ionization chamber through the isotope exchange reaction 2 between water on piping surface and HTO in purge gas is liberated when the humidified gas with no tritium is applied to the piping system. In the case of hydrogen purge to $LiAlO_2$, the amount of tritium trapped to the piping surface becomes smaller than the case of dry N_2 purge in Fig. 3 as compared with and Fig. 4. It is considered that the portion

Table 1
Comparison of surface reactions on grain of solid breeder materials related to release of bred tritium

	Dry purge gas	Purge gas with hydrogen	Purge gas with water vapor
∼573 K	Adsorption/desorption	Adsorption/desorption	Isotope exchange 2 Adsorption/desorption
573–773 K	Adsorption/desorption	Adsorption/desorption Water formation Isotope exchange 2 Isotope exchange 1	Isotope exchange 2 Adsorption/desorption
773–973 K	Adsorption/desorption	Adsorption/desorption Water formation Isotope exchange 2 Isotope exchange 1 Surface condition change	Isotope exchange 2 Adsorption/desorption
∼973 K	Adsorption/desorption	Adsorption/desorption Water formation Isotope exchange 1 Isotope exchange 2 Surface condition change	Isotope exchange 2 Adsorption/desorption

of tritium converted to the HT form increases and water from water formation reaction decreases the HTO/H_2O ratio at addition of hydrogen to the purge gas because tritium release from $LiAlO_2$ occurs at high temperature. Then, tritium trapped to the piping surface at room temperature through the isotope exchange reaction 2 becomes smaller.

The isotope exchange reaction 1 gives almost no contribution at the low temperature even when 1000–10 000 ppm of hydrogen is added to the purge gas because its reaction rate observed for Li_2TiO_3, Li_4SiO_4, Li_2ZrO_3, $LiAlO_2$ or Li_2O is so slow at the temperature lower than 600 K [10,11]. On the contrary, the isotope exchange reaction 2 works effectively to remove tritium from the grain surface as HTO even when only a small amount of water vapor is included in the purge gas because its reaction rate is large even at the room temperature [8]. At the same time, tritium trapped on the grain surface is released as the form of HTO through desorption reaction according to the adsorption isotherm of physically adsorbed water. Accordingly, at the lower temperature than 600 K the main chemical form of released tritium to the purge gas is considered to be HTO. At the higher temperature of breeder bed, the composition of HT is supposed to increase because the reaction heat of the isotope exchange reaction 1, 120–170 kJ/mol, is much larger than that of the isotope exchange reaction 2, almost no temperature dependency [8,10,11]. The water formation reaction, however, becomes vigorous on the grain surface at the higher temperature than 750 K to supply water to the purge gas. This phenomenon makes the HTO composition larger through increase of water vapor to accelerate the isotope exchange reaction 2.

Observations above indicate that the mass transfer resistance due to reactions on the grain surface becomes smallest when the humidified purge gas is applied. Number of surface reactions required to be taken into account in model formation for quantification of release curve of bred tritium is also smaller in the case when the humidified purge gas is applied. Then, it is recommended to use the release curve obtained at purge by water vapor for estimation of tritium diffusivity by curve fitting method where the isotope exchange reaction 2 and desorption give the contribution as the surface phenomena to the overall mass transfer resistance at release of bred tritium to the purge gas. Comparison of the fitting curve with the observed release curve is shown in Fig. 6 for the case where an irradiated $LiAlO_2$ sample was purged by N_2 gas with 10 000 ppm water vapor. The sample irradiated only for 3 min was taken for the fitting object in this figure expecting that irradiation for 3 min did not create enough defects to give effect on tritium diffusion. The modified method [15] of the way proposed by Beloglazov et al. for Li_2ZrO_3 [12] was applied in this study taking the isotope exchange capacity on the grain surface and a good fitting was obtained as shown in Fig. 6. Then, the following equation is obtained to represent the effective diffusivity of bred tritium in crystal grain of $LiAlO_2$ in this study.

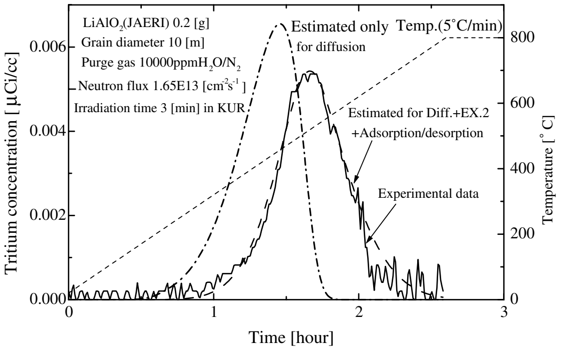

Fig. 6. Comparison of fitting curve with observed release curve.

$$D_T = 2.5 \times 10^{-7} \exp(-110\ [\mathrm{kJ}]/RT)\ (\mathrm{m^2/s}). \qquad (1)$$

D_T is called the effective diffusivity because this parameter represents the whole migration behavior in bulk of the grain.

This equation gives the larger diffusivity than any other diffusivity presented so far by various authors [16–21] as compared in Fig. 7 because the mass transfer resistance at the grain surface is expected to be eliminated in the estimation procedure of this study. Other diffusivities compared in this figure may include the effect of surface reactions because they were mainly estimated from the release curve obtained at 1000 ppm hydrogen purge considering that diffusion in $LiAlO_2$ grain control the tritium release.

The tritium release curve estimated for the case when diffusion is hypothetically considered to be the rate

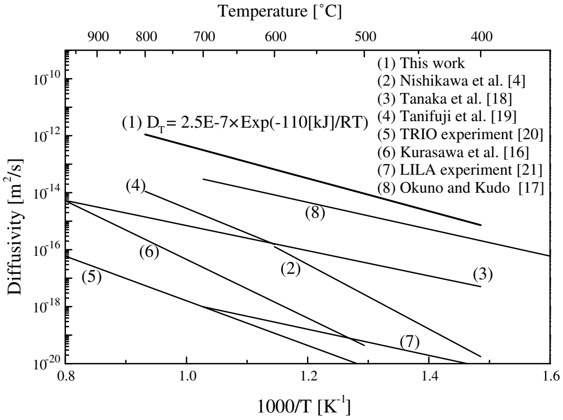

Fig. 7. Diffusivity of bred tritium in $LiAlO_2$ reported by various authors.

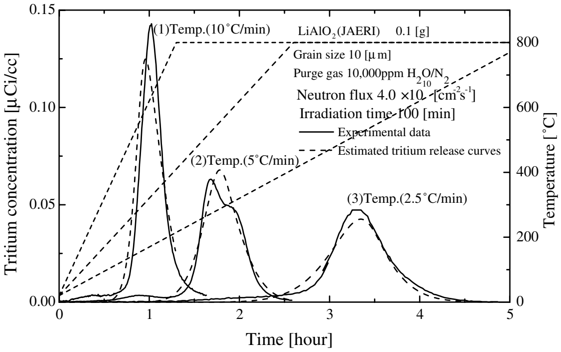

Fig. 8. Comparison of estimated tritium release curves with observed values.

controlling step is also shown in Fig. 6 where the diffusivity obtained in this study is used. Comparison of two estimated curves in Fig. 6 shows difference in shape and initiation time of release, and these differences imply that effect of surface phenomena cannot be ignored even at the case where the purge gas with water vapor is applied to $LiAlO_2$ which is believed to have the much smaller diffusivity than Li_2TiO_3, Li_2ZrO_3, Li_4SiO_4 or Li_2O.

Comparison of estimated tritium release curves with observed values are shown in Fig. 8 where the rising rate of temperature was varied at release of bred tritium from $LiAlO_2$ irradiated for 100 min. The estimated release curve using the diffusivity shown by Eq. (1) gives satisfactory agreement for each case. This comparison also implies that the irradiation time within 100 min does not give remarkable difference in tritium migration behavior through $LiAlO_2$ grain.

It is necessary to keep the over-all tritium breeding ratio larger than 1.0 for development of a D–T fusion reactor having the self sustained fuel cycle. From this viewpoint, tritium bred in the blanket must be recovered with high efficiency. Then, understanding about the chemical composition of the bred tritium released to the blanket purge gas is important for design of the recovery system and for estimation of tritium permeation to the outer region of the fuel system. Experimental results of this study indicate that further quantitative discussion about the chemical composition of the bred tritium is required because it is revealed in this study that not a few portion of bred tritium can be released from $LiAlO_2$ as the HTO form even when the purge gas with hydrogen is applied.

5. Conclusions

The release behavior of bred tritium from $LiAlO_2$ was discussed applying the out-pile temperature programmed desorption method and the following conclusions were obtained.

1. Mass transfer resistance due to the surface phenomena on grain gives profound effect on the release behavior of tritium and this effect becomes small when water vapor is added to the purge gas.
2. The equation for the effective diffusivity of tritium in the $LiAlO_2$ grain is obtained as follows applying the curve fitting method to the release curve obtained at purge by humidified nitrogen. Isotope exchange reaction 2 and desorption reaction at grain surface are taken into account together with diffusion in bulk of grain in this estimation.

$$D_T = 2.5 \times 10^{-7} \exp(-110\ [\mathrm{kJ}]/RT)\ (\mathrm{m}^2/\mathrm{s}). \qquad (2)$$

   This equation gives the larger diffusivity than any other diffusivity presented so far by various authors because the mass transfer resistance at the grain surface is eliminated in this estimation.
3. Not a few portion of bred tritium is released to the purge gas in the form of HTO from a $LiAlO_2$ bed even when hydrogen is added to the purge gas. This observation implies that it is necessary to have a bred tritium recovery system effective for both tritium in HT and HTO form.

References

[1] M. Nishikawa, Y. Kawamura, K. Munakata, H. Matsumoto, J. Nucl. Mater. 174 (1990) 121.
[2] Y. Kawamura, M. Nishikawa, T. Shiraishi, K. Okuno, J. Nucl. Mater. 230 (1996) 287.
[3] N. Nakashima, S. Beloglazov, K. Hashimoto, M. Nishikawa, Fusion Sci. Technol. 41 (2002) 1044.
[4] M. Nishikawa, A. Baba, Y. Kawamura, J. Nucl. Mater. 246 (1997) 1.
[5] M. Nishikawa, A. Baba, J. Nucl. Mater. 257 (1998) 162.
[6] K. Hashimoto, M. Nishikawa, N. Nakashima, S. Beloglazov, M. Enoeda, Fusion Eng. Des. 61&62 (2002) 375.
[7] M. Nishikawa, T. Takeishi, Y. Matsumoto, I. Kumabe, Nucl. Instrum. and Meth. A 278 (1988) 525.
[8] N. Nakashio, M. Nishikawa, Fusion Technol. 33 (1998) 287.
[9] M. Nishikawa, N. Nakashio, T. Shiraishi, S. Odoi, T. Takeishi, K. Kamimae, J. Nucl. Mater. 277 (2000) 99.
[10] A. Baba, M. Nishikawa, T. Eguchi, J. Nucl. Mater. 250 (1997) 29.
[11] A. Baba, M. Nishikawa, T. Eguchi, T. Kawagoe, Fusion Eng. Des. 49&50 (2000) 483.
[12] S. Beloglazov, M. Nishikawa, T. Tanifuji, Fusion Sci. Technol. 41 (2002) 1049.
[13] M. Nishikawa et al., Fusion Sci. Technol. 41 (2002) 1025.
[14] M. Nishikawa, T. Kinjyo, Y. Nishida, T. Tanifuji, J. Nucl. Mater. 325 (2004) 87.

[15] T. Kinjyo, M. Nishikawa, Y. Nishida, in: Proceedings of the 11th International Workshop on Ceramic Breeder Blanket Interactions, December 15–17, Tokyo, Japan, 2003.

[16] T. Kurasawa, H. Watanabe, G.W. Hollenberg, J. Nucl. Mater. 155–157 (1988) 544.

[17] H. Kudo, K. Okuno, J. Nucl. Mater. 155–157 (1988) 524.

[18] S. Tanaka et al., Fusion Eng. Des. 8&9 (1989) 155.

[19] T. Tanifuji et al., Presented at Annual Meeting of Atomic Society of Japan, 1990.

[20] R.G. Clemmer et al., J. Nucl. Mater. 133&134 (1985) 171.

[21] M. Briec et al., J. Nucl. Mater. 155–157 (1988) 549.