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Chemical form of tritium released from solid breeder materials

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Abstract

The fraction of HTO in total tritium was measured at release of the bred tritium to the purge gas with hydrogen using the thermal release after irradiation method, where neutron irradiation was performed at the Japan Research Reactor-3 (JRR-3) in Japan Atomic Energy Research Institute (JAERI) or the Kyoto University Research Reactor (KUR reactor) in Kyoto University. It is experimentally confirmed in this study that not a small portion of bred tritium is released to the blanket purge gas in the form of HTO from ceramic breeder materials even when hydrogen is added to the purge gas. Observation in this study implies that it is necessary to have a bred tritium recovery system useful for both HT and HTO form tritium. The water formation properties from Li_2TiO_3 bed placed in the hydrogen atmosphere were also discussed in this study.

1. Introduction

It is required to develop an efficient tritium fueling cycle keeping the over-all tritium breeding ratio larger 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, design of efficient means to recover bred tritium with minimum permeation loss is to be made. Tritium behavior in the breeding blanket is discussed in this paper targeting at the chemical form of tritium at release of bred tritium to blanket purge gas from solid breeder materials because the chemical form of tritium in the blanket purge gas gives profound effect on design of tritium recovery means and at estimation of permeation loss.

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 the fastest surface reaction among reactions considered to take place at release of bred tritium from solid breeder blanket such as absorption, adsorption and desorption, isotope exchange reaction between tritium on grain surface and hydrogen in gas phase (named as the isotope exchange reaction 1) [4–6].

In this study the fraction of HTO in total tritium was measured at release of the bred tritium to the purge gas with hydrogen using the thermal release after irradiation method, where neutron irradiation was performed at the

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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 water formation properties from a Li_2TiO_3 bed placed in the hydrogen atmosphere was also discussed in this study.

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,
(10) transfer of hydrogen isotopes and water through boundary layer formed on the surface of a sintered pebbles to the gas stream.

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. Tritium release behavior from a blanket material at low temperature is considered to be strongly affected by these tritium transfer steps. 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), (6–8) 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), (6–8). 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 results on tritium inventory obtained so far indicates 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 purge gas.

Above considerations indicate that a certain part of the bred tritium must be released from a blanket material to the purge gas as the chemical form of HTO. Accordingly, it is necessary to check if the fraction of HTO in bred tritium is negligible or not in design of the bred tritium recovery system.

3. Experimental

Release curves of bred tritium from various ceramic breeder materials such as Li_4SiO_4, Li_2TiO_3, Li_2ZrO_3 or $LiAlO_2$ were obtained applying the out-pile temperature programmed desorption method using the experimental apparatus of which schematic diagram is shown in Fig. 1. 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 the KUR reactor in Kyoto University. The flux of thermal neutron was 4.0×10^{13} and $1.6–2.8\times10^{13}$ $n/cm^2\,s$ in JAERI and KUR, respectively. The irradiated sample was purged by N_2 gas with hydrogen of various partial pressures, and the temperature of the sample bed was changed linearly from room temperature to 1073 K with the rising rate of 5 K/min. The flow rate of the purge gas

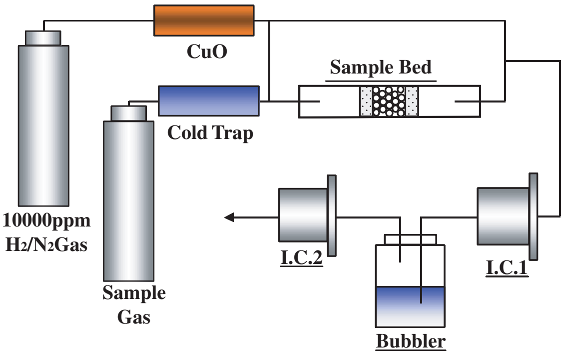

Fig. 1. Schematic diagram of experimental apparatus for measurement of tritium release characteristic.

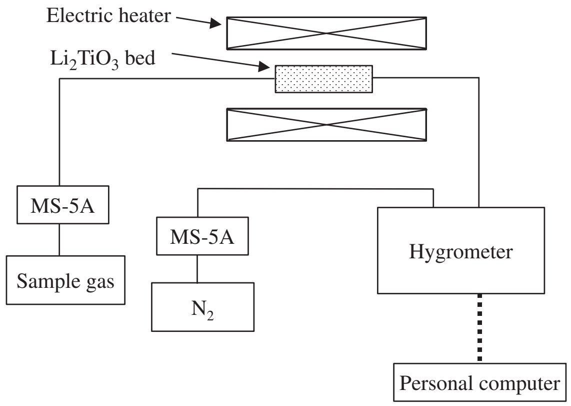

Fig. 2. Schematic diagram of experimental apparatus for measurement of water formation characteristic.

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. 1 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 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 is considered to be negligible when 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].

The schematic diagram of the experimental apparatus for measurement of the water formation capacity in the Li_2TiO_3 bed is shown in Fig. 2. The amount of water formed was measured using a hygrometer.

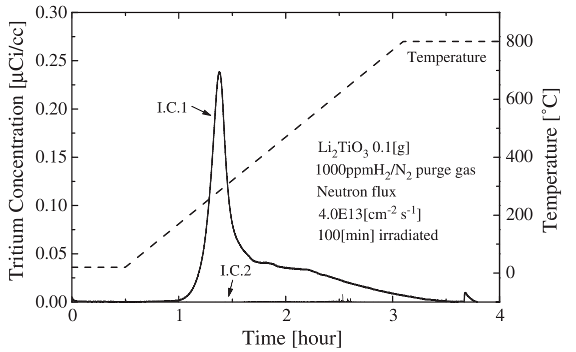

Fig. 3. Tritium release from Li_2TiO_3 bed purged by 1000 ppm hydrogen.

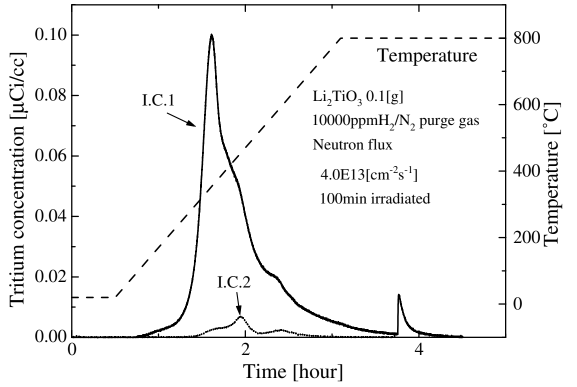

Fig. 4. Tritium release from Li_2TiO_3 bed purged by 10 000 ppm hydrogen.

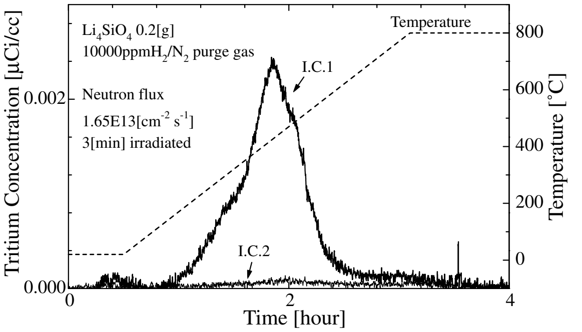

Fig. 5. Tritium release from Li_4SiO_4 bed purged by 10 000 ppm hydrogen.

4. Results and discussion

The release curves of total tritium and tritium of HT form observed for Li_4SiO_4 (grain size 1.2 μm, pebble size 0.5 mm, made by Forshungszentrum Karlsruhe (FzK)), Li_2TiO_3 (grain size 1 μm, pebble size 1 mm, made by Commissariat a L'Energie Atomique (CEA)), Li_2ZrO_3 (grain size 13 μm, pebble size 1 mm, made by Mitsubishi atomic power industry (MAPI)) and $LiAlO_2$ (grain size 10 μm, pebble size 4.0 mm, made by JAERI) are compared in Figs. 3–6, respectively, where the N_2 gas with 1000 or 10 000 ppm hydrogen is used as the purge gas. It can be seen from Figs. 3–7 that most bred tritium from Li_4SiO_4, Li_2TiO_3 and Li_2ZrO_3 is released as HTO though most tritium is released as HT from $LiAlO_2$ in the condition of this experiment and it is also observed that the fraction of HT in the released tritium

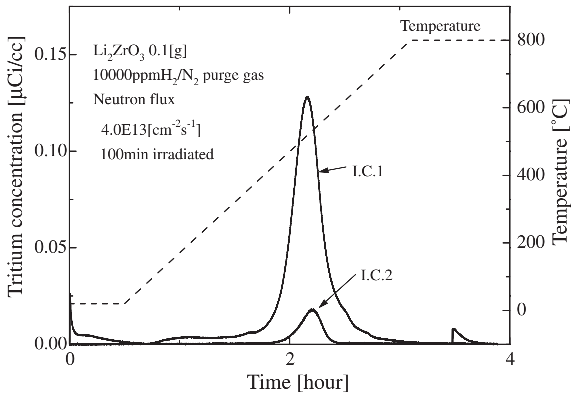

Fig. 6. Tritium release from Li_2ZrO_3 bed purged by 10 000 ppm hydrogen.

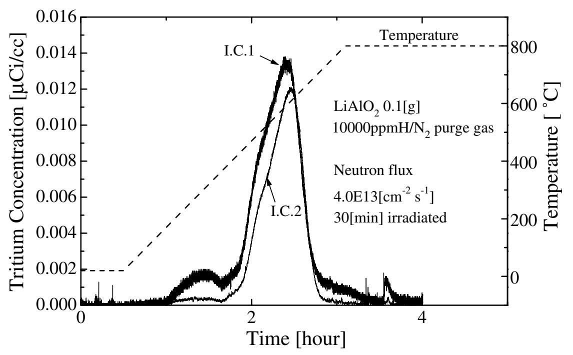

Fig. 7. Tritium release from $LiAlO_2$ bed purged by 10 000 ppm hydrogen.

increases with rise of the temperature. It is known from comparison of Fig. 4 with Fig. 5 that the higher hydrogen concentration in the purge gas gives the higher HT ratio. It is considered by the present authors that competition of water desorption reaction of tritium as HTO, isotope exchange reaction 1 to produce HT and isotope exchange reaction 2 to produce HTO decide the ratio of HTO to HT [4,5].

It is shown in Figs. 3–7 that some tritium is quickly liberated soon after switch of the purge gas from N_2 with hydrogen to humidified N_2 after the purging procedure of irradiated sample by 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. 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.

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.

The isotope exchange reaction 1 gives almost no contribution at 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. At the same time, tritium trapped on the grain surface is released as the form of HTO through desorption

Table 1
Comparison of surface reactions on grain of solid breeder materials at various temperature

	Room temperature ∼573 K	573–773 K	773–973 K	973 K∼
Dry purge gas	Adsorption/desorption	Adsorption/desorption	Adsorption/desorption Li liberation	Adsorption/desorption Li liberation
Purge gas with hydrogen	Adsorption/desorption	Adsorption/desorption Water formation Isotope exchange 2 Isotope exchange 1	Adsorption/desorption Water formation Isotope exchange 2 Isotope exchange 1 Li liberation Surface condition change	Adsorption/desorption Water formation Isotope exchange 1 Isotope exchange 2 Li liberation Surface condition change
Purge gas with water vapor	Isotope exchange 2 Adsorption/desorption Li liberation (Li_2O)	Isotope exchange 2 Adsorption/desorption Li liberation (Li_2O)	Isotope exchange 2 Adsorption/desorption Absorption (Li_2O) Li liberation	Isotope exchange 2 Adsorption/desorption Absorption (Li_2O) Li liberation

Table 2
Comparison of tritium release characteristic from solid breeder materials

Breeder material	Li_2TiO_3 (CEA)	Li_2TiO_3 (CEA)	Li_4SiO_4 (FzK)	Li_2ZrO_3 (MAPI)	$LiAlO_2$ (JAERI)
Purge gas	10 000 ppm H_2/N_2	1000 ppm H_2/N_2	10 000 ppm H_2/N_2	10 000 ppm H_2/N_2	10 000 ppm H_2/N_2
Irradiated place	JAERI	JAERI	KUR	JAERI	JAERI
Neutron flux ($cm^{-2}\,s^{-1}$)	4×10^{13}	4×10^{13}	1.6×10^{13}	4×10^{13}	4×10^{13}
Irradiation time	100 min	100 min	3 min	100 min	30 min
Theoretical tritium breeding amount (μCi)	875.8	875.8	39.74	629.66	281.09
Beginning of tritium release (min)	80–90	70–80	100	100–110	1st: 60–70 2nd: 110–120
Temperature giving peak in release curve (°C)	360	280	430	520	1st: 300 2nd: 590
Tritium amount counted by I.C.1 (μCi)	717.84	1114.56	20.4	625.92	113.4
Tritium amount counted by I.C.2 (μCi)	64.32	24.12	1.91	64.32	79.2
Tritium (I.C.2)/Tritium (I.C.1)	0.0896	0.0216	0.0938	0.1028	0.6984

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 form. 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 is much larger than that of the isotope exchange reaction 2 [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 lager through increase of water vapor to accelerate the isotope exchange reaction 2 and decrease of hydrogen in the purge gas to deccelerate the isotope exchange reaction 1. It has been reported by the present authors that change of the surface condition of Li_2TiO_3 due to water formation reaction with hydrogen gives the drastic decrease of reaction rate of isotope exchange reaction 1 [3,6]. This observation implies that composition of HT may not increase at the higher temperature in the Li_2TiO_3 blanket purged with the gas containing hydrogen.

The observed results compared in Figs. 3–7 and in Table 2 well correspond to the predictions stated above.

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], and the water formation capacity is decided as the amount of water generated from a mol of solid breeder material. An example of water formation from a packed bed of Li_2TiO_3 is shown in Fig. 8, where N_2 gas with 1640 ppm hydrogen was introduced and the bed temperature was changed in stepwise. The water formation capacity obtained in this study for Li_2TiO_3 (grain size 18 μm, pebble size 1 mm, made by Kawasaki Heavy Industry (KHI)) is compared in Fig. 9 with the capacity observed for other blanket materials elsewhere [2]. This figure indicates that Li_2TiO_3 have the largest water formation capacity among five solid breeder materials experimented in this study. The water formation capacity observed for Li_2TiO_3 of smaller grain size (grain size 1 μm, pebble size 1 mm, made by CEA) gives the twice to three times larger water formation capacity observed for Li_2TiO_3 from KHI. The water formation capacity should be same regardless of the grain diameter if the whole bulk of Li_2TiO_3 grain give contribution to water formation, and the water formation capacity should be somehow proportional to the specific surface area if only the thin film formed at the grain surface gives contribution to the water formation reaction. The observed ratio of twice to

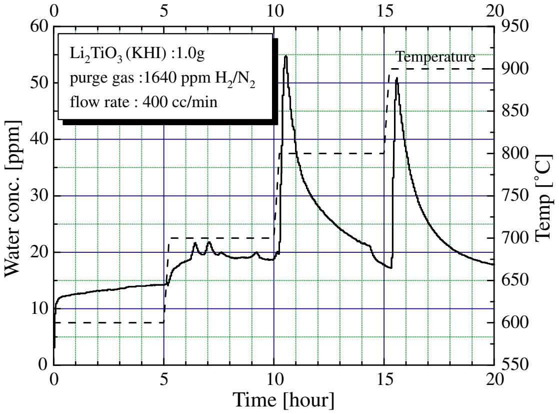

Fig. 8. Example of water release curve from Li_2TiO_3 bed at purge using N_2 with hydrogen.

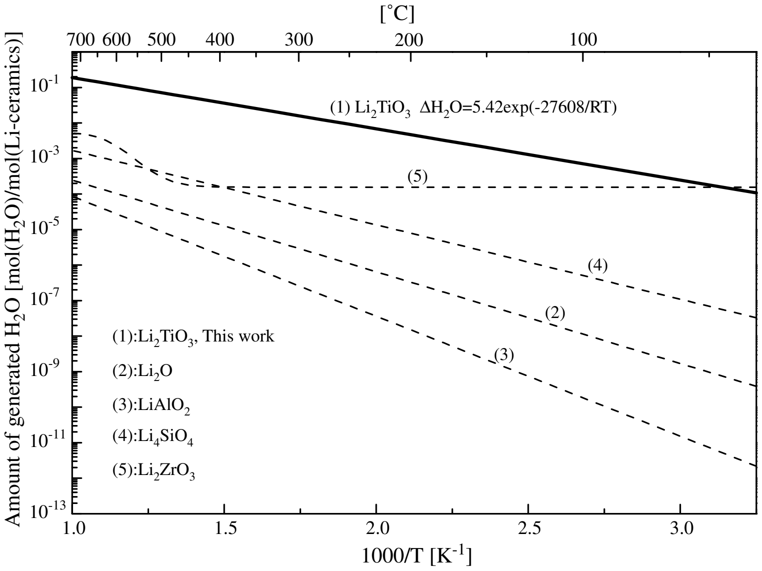

Fig. 9. Comparison of water formation capacity for various solid breeder materials.

three times implies that the thickness of the film that liberates oxygen to form water is 1.2–1.5 μm. This means that whole of a 1 μm grain from CEA contributes to the water formation reaction, though only a part contributes in the case of a 18 μm grain from KHI. The observation stated above indicates that a blanket with 550 tons of Li_2TiO_3 (containing 70 tons of Li, grain size of Li_2TiO_3 is 18 or 1 μm) has the water formation capacity of 50 000 or 100 000 mol of water, respectively, as a whole. Considering that the tritium breeding rate is about 70 mol/day in a 1 GWe Tokamak type D–T fusion reactor, water formation reaction is anticipated to give effect on the chemical composition of bred tritium released to the purge gas especially at the earlier stage of operation using high temperature blanket.

It is necessary to keep the over-all tritium breeding ratio larger than 1.0 to develop 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 small amount of tritium can be released from solid breeder materials as the HTO form even when the purge gas with hydrogen is applied.

One solution is to have a precious metal catalyst bed at the outlet of the blanket purge gas to convert HTO to HT with help of the isotope exchange reaction 1 as proposed by the present authors elsewhere [6].

5. Conclusion

It is experimentally confirmed in this study that not a small portion of bred tritium is released to the purge gas in the form of HTO from ceramic breeder materials even when hydrogen is added to the purge gas. The chemical composition is decided by the competitive reaction at the surface of solid breeder materials where desorption reaction, isotope exchange reaction 1, and isotope exchange reaction 2 take part. The water formation reaction at addition of hydrogen also plays a role to increase the ratio of HTO.

Li_2TiO_3 gives the largest water formation capacity among solid breeder materials experimented in this study.

Observation in this study implies that it is necessary to have a bred tritium recovery system useful for both HT and HTO form tritium.

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. 30 (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.