Change of tritium species in Li_2BeF_4 molten salt breeder under neutron irradiation at elevated temperature

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Abstract

The mechanism of the change of tritium chemical species from T^+ to HT in Flibe (Li_2BeF_4) a potential liquid tritium breeding material under He + H_2 purge gas was investigated by an in situ tritium release experiment. In case of low H_2 partial pressure, the temporal change in HT release rate from Flibe has a dependence on the H_2 partial pressure. The concentrations of four kinds of species, T^+, HT, H_2 and H^+ dissolved in Flibe control the rate of the change of the tritium chemical species in Flibe. It is considered that, at the steady-state in the case of low H_2 partial pressure, TF becomes the main chemical form of released tritium by decreasing the rate of the change of the tritium chemical species, which is caused mainly by the decrease of H_2 concentration in Flibe. This decrease of H_2 concentration is considered to be much larger in an actual blanket. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Various candidate materials have been considered for the tritium breeding material in the Controlled Thermonuclear Reactor system (CTR). Among those, molten salt has many advantages, such as no radiation damage, high chemical stability, easy maintenance, possible use as a coolant and low electrical conductivity to reduce the pressure drop caused by the magnetohydrodynamics (MHD) effect. The 2:1 molten mixture of lithium fluoride and beryllium fluoride ($2LiF–BeF_2$ denoted as Flibe) is a prominent salt, because of its high tritium breeding ratio and large fluidity. Actually, it is utilized in some conceptual designs for liquid blankets such as High-Yield Lithium Injection Fusion-Energy II (HY-LIFE-II) [1] and Force-Free Helical Reactor (FFHR) [2]. Critical issues in a Flibe blanket system are the corrosive behavior of tritium fluoride (TF) generated by the nuclear reaction of LiF with neutrons, and possible tritium permeation through the structural materials from Flibe or from the gas phase containing tritium. Many physical and chemical properties of Flibe have

already been made clear in the studies of Molten Salt Breeding Reactor (MSBR) in 1960s, but there are only a few studies on tritium behavior in Flibe and in the structural material; this information is necessary to design a breeding system in the CTR. Because the tritium behavior has a possibility to change under irradiation, it is very important to understand tritium behavior in the Flibe under neutron irradiation at elevated temperatures. Tritium release behavior from molten Flibe under neutron irradiation strongly depends on the chemical form of tritium. The main chemical forms of released tritium are HT and TF [3,4], which are different in chemical behavior from each other, e.g., the difference between the mass transfer coefficients of these chemical species from Flibe to the gas phase [5]. The isotopic exchange reaction of TF with H_2 may generate HT [6], because the change of chemical forms depends on H_2 activity and HF activity in the experimental system [7]. Three tritium transfer processes are considered [7]: process (1) is the direct release of generated T^+ to the purge gas as TF, process (2) is the conversion from T^+ to HT, and process (3) is the release of HT to the purge gas. In this paper, we make some in-pile tritium release experiments from Flibe to gas phase, focusing on the case of process (2) being dominant for tritium release, and study about mechanism of the isotopic exchange reaction in Flibe.

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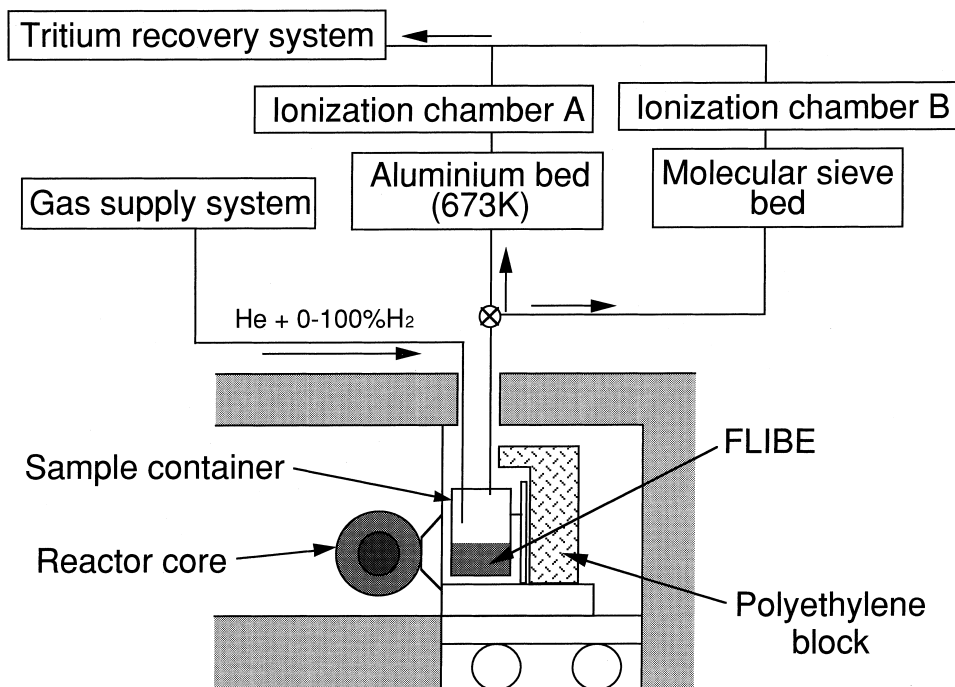
Fig. 1. Apparatus for in-pile tritium release experiment.

2. Experimental

The in situ tritium release experiment was performed using the apparatus shown in Fig. 1, which consisted of a purge gas supply system, an in-reactor component, two sets of tritium monitoring systems and a tritium recovery system. The in-reactor component was placed in an irradiation position of the fast neutron source reactor "YAYOI" of the University of Tokyo with the neutron flux of 10^8–10^9 n/cm^2 s. Tritium was generated in the specimen at a rate of about 40 Bq/s g-Li, released from the specimen as HT or TF, and swept by a purge gas (He + H$_2$) flowing over the specimen at the rate of about 100 cm^3/s to the monitoring systems.

The tritium containing purge gas was divided in two lines: one had an aluminum reduction bed at 673 K and the other had a molecular sieve bed. The condensable species (TF) was converted to non-condensable species (HT) in the aluminum reduction bed and the concentration of all the released tritium species (HT and TF) was monitored by the ionization chamber A. On the other hand, TF was captured in the molecular sieve bed and only the HT concentration was monitored by the ionization chamber B. Thus, the temporal change of tritium release rate could be determined continuously by separating TF and HT. The in-reactor components consisted of a sample container, a sheathed heater, a thermal insulator, a thermocouple and an Monel crucible, as shown in Fig. 2. The sample container was made

of Monel metal (Ni70%–Cu30%), which has a high tolerance for fluoric acid at high temperatures, and the tubing used at room temperature was made of Teflon to avoid the change of the tritium chemical form. About 235 g of Flibe supplied from Furuchi was dried at 623 K
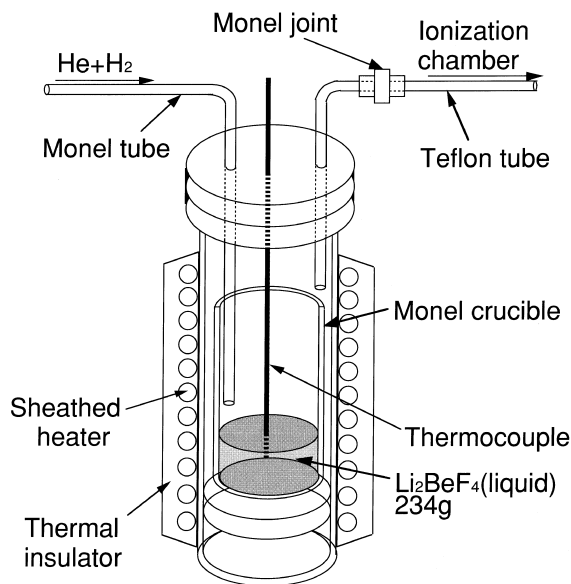

Fig. 2. Cross-section of Monel sample container.

for two days in the Monel crucible (58 mm in inner diameter, 200 mm in inner depth and 3 mm in thickness) installed in the sample container.

Because we focus on the HT release, the partial pressure of H_2 was controlled to make HT release. HT, one of the chemical forms of released tritium, was released even under He + 10 ppm H_2 purge gas, unless the sample was not dried enough nor HF was added to the purge gas. In the following experiment, the chemical form of released tritium was only HT and no TF was observed in about 150 min after the start of the reactor (the reactor is shut down after 150 min). We measured the chemical form and the temporal change of the HT release rate with changing H_2 partial pressure in the purge gas.

3. Results and discussion

3.1. Model of tritium chemical change in Flibe

From the results in this experiment and previous work, we consider the tritium release mechanism to construct a tritium release model, shown in Fig. 3. Thermal neutrons from the reactor core react with Li^+ in Flibe to generate T^+. Some T^+ combining electrically with F^- release directly as TF to the purge gas. We call

this process process (1) and the mass transfer rate of the process (1) $R(1)$. $R(1)$ is expressed as

$$R(1) = K_{TF}([TF] - [TF]_g), \tag{1}$$

where K_{TF} is the mass transfer coefficient of TF containing the volume and surface area of the sample, [A] means the concentration of species A in Flibe, and $[A]_g$ means the partial pressure of species A in the purge gas expressed by the corresponding concentration in liquid Flibe using the solubility of A in Flibe. $[TF]_g$ is considered to be much smaller than [TF] in Eq. (1), because the purge gas always remove released TF gas from the sample container. In addition, the concentration of TF in Flibe equals to the concentration of T^+ because TF perfectly dissociates into T^+ and F^- in Flibe. Therefore, Eq. (1) is expressed as

$$R(1) = K_{TF}[T^+]. \tag{2}$$

The rest of the generated T^+ reacts with H_2 dissolved in Flibe as

$$T^+ + H_2 \rightarrow HT + H^+. \tag{3}$$

This process (2) is characterized by the rate of the isotopic exchange reaction $R(2)$ and this parameter is expressed by the equation:

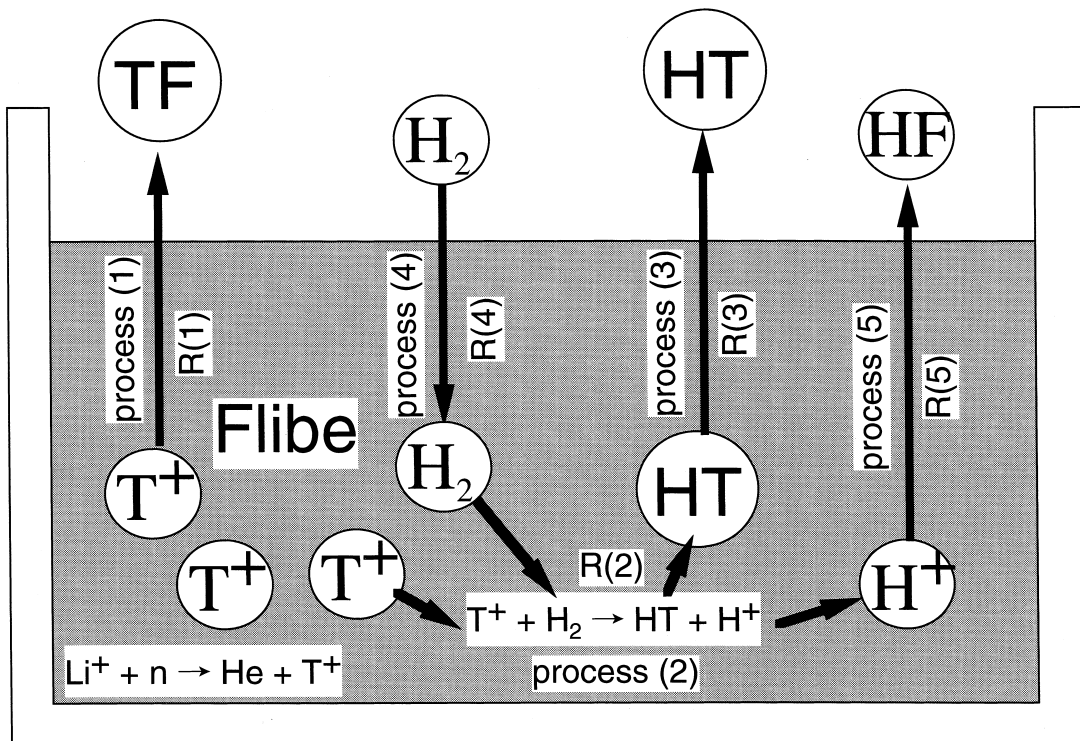$$R(2) = k_1[T^+][H_2] - k_2[H^+][HT], \tag{4}$$

Fig. 3. Mechanism of tritium release from Flibe.

where k_1 and k_2 are constants. HT generated by the reaction of process (2) releases to the gas phase by process (3) at the rate of $R(3)$. In order to promote the process (2), H_2 is supplied from the gas phase to Flibe at the rate of $R(4)$. And H^+ generated by the process (2) releases from Flibe to the gas phase at the rate of $R(5)$.

$$R(3) = K_{HT}[HT], \tag{5}$$

$$R(4) = K_{H_2}([H_2]_g - [H_2]), \tag{6}$$

$$R(5) = K_{HF}[H^+], \tag{7}$$

where K is the mass transfer coefficient containing the volume and the surface area of the sample, and $[HT]_g$ for $R(4)$ and $[H^+]_g$ for $R(5)$ are already neglected in the equals.

Then, in this model, the temporal changes of the concentrations of the four kinds of species are important to predict the isotopic exchange behavior:

$$\frac{d[T^+]}{dt} = G - R(1) - R(2), \tag{8}$$

$$\frac{d[H_2]}{dt} = R(4) - R(2), \tag{9}$$

$$\frac{d[HT]}{dt} = R(2) - R(3), \tag{10}$$

$$\frac{d[H^+]}{dt} = R(2) - R(5), \tag{11}$$

where G is T^+ generation rate by the reaction of Li^+ with neutron and t is the time after the start of the tritium generation. The initial conditions in our experimental system are

$$[T^+] = 0, \quad [H_2] = [H_2]_g, \quad [HT] = 0,$$
$$\text{and } [H^+] = 0 \qquad \text{at } t = 0. \tag{12}$$

In order to solve the above equations six rate constants (K_{TF}, k_1, k_2, K_{HT}, K_{H_2} and K_{HF}) related to the behavior of hydrogen-containing species in Flibe are necessary, but we know only the values of the one parameter K_{HT} in our experimental system. Therefore, we introduce two assumptions; K_{TF} equals to K_{HF} and K_{HT} equals to K_{H_2}, because the two molecules of each combination have the same chemical property. With these assumptions, Eqs. (13) and (14) are obtained by adding Eq. (8) to Eq. (11) and Eq. (9) to Eq. (10).

$$\frac{d[T^+]}{dt} + \frac{d[H^+]}{dt} = G - K_{TF}([T^+] + [H^+]), \tag{13}$$

$$\frac{d[H_2]}{dt} + \frac{d[HT]}{dt} = K_{HT}[H_2]_g - K_{HT}([H_2] + [HT]). \tag{14}$$

Therefore, these equations are conducted;

$$[T^+] + [H^+] = G/K_{TF}(1 - \exp(-K_{TF}t)), \tag{15}$$

$$[H_2] + [HT] = [H_2]_g. \tag{16}$$

3.2. Release rate of HT release

As shown in Fig. 4, in the case of the H_2 purge gas, the He + 10%H_2 purge gas and the He + 1%H_2 purge gas, the temporal change of HT release rate did not depend on the partial pressure of H_2 in the purge gas at 873 K. But in the case of the He + 0.1%H_2 purge gas, the He + 0.01%H_2 purge gas and the He + 0.001%H_2 purge gas, the temporal change of HT release rate of tritium was always lower than the case of the He + (1–100%)H_2 purge gas and the decrease of the release rate depended on the decrease of the partial pressure of H_2 in the purge gas. This indicates, the mechanisms of tritium release are different between the cases of H_2 partial pressures over and under 1000 Pa.

In the cases of the H_2 partial pressure over 1000 Pa, the fitting curves for the temporal change of HT release rate in the Fig. 4 assume a time lag of first-order and that the release rates at the steady-state equal to the tritium generation rate. Ref. [8] insists that in this case all tritium release from Flibe proceeds through the series of process (2) and process (3) and that the rate-determining process of tritium release is the HT diffusion in the thin liquid film of Flibe (process (3)).

In the cases of the H_2 partial pressure under 1000 Pa, we select the fitting curves for the temporal change of HT release rate in the Fig. 4 assuming the same time lag of first-order as that in the cases of the high H_2 partial pressure and that the rates at the steady-state does not equal to the tritium generation rate. The former assumption indicates that the HT release has the same mass-transfer coefficient in the cases of the low H_2 partial pressure as well as in the cases of the high H_2 partial pressure, which means HT releases through the same route (process (2) + (3)) and the rate-determining process of HT release is the HT diffusion in the thin Flibe liquid film in the both cases. The later indicates that in the cases of the low H_2 partial pressure rest of the tritium releases through another route (process (1)) to release TF at the steady-state and that the mass transfer coefficient of process (1) is too small to be determined in 150 min. Therefore, at the steady-state in the case of the low H_2 pressure, a part of generated tritium is released as HT through process (2) + (3) and the other tritium is considered to be released as TF through process (1). Table 1 shows the release rate of the chemical forms of tritium at the steady-state under each H_2 pressure in this experimental system. The chemical form of released tritium is HT and no TF would be observed under He + 1%H_2 purge gas, while under He + 0.1%H_2 purge gas, the main chemical form of released tritium is drastically changed to be TF.
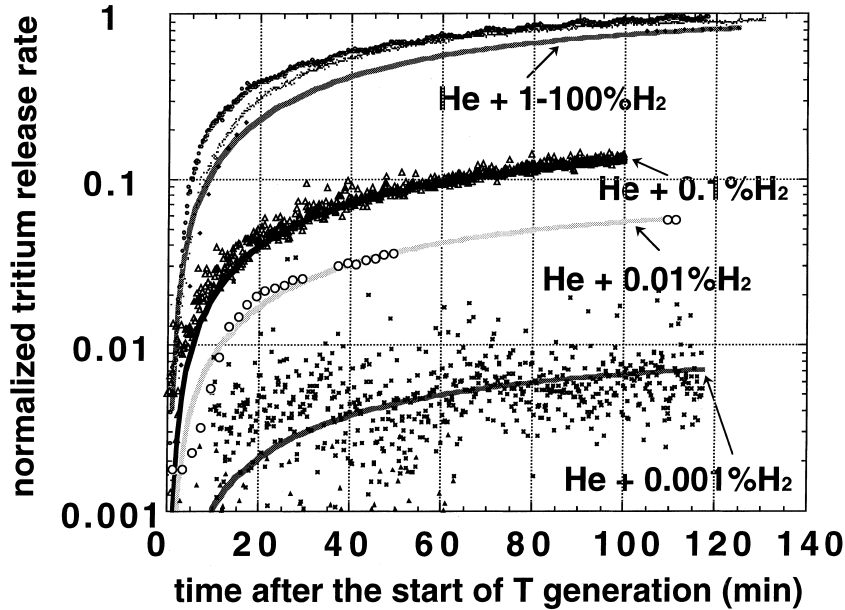
Fig. 4. Tritium transfer rate in HT release.

Table 2 shows the HT concentration in Flibe at the steady-state calculated by Eq. (5) with the experimental data on R(3) and K_{HT}, and the H_2 concentration in Flibe at the steady-state calculated by Eq. (16). In the cases of the high H_2 partial pressure the H_2 concentration is much higher than the HT concentration, while in the case of the He + 0.1%H_2 purge gas about 20% of the hydrogen molecules in Flibe exist as HT, and in the case of the He + 0.001%H_2 purge gas, it is about 86%. Thus,

as the H_2 partial pressure in the purge gas become lower, the H_2 concentration which promotes process (2) to generate HT decreases rapidly, and the HT concentration which prevents process (2) to generate HT increases. In other words, the concentration of H_2 molecules in Flibe is enough to promote process (2) in the cases of the high H_2 partial pressure, but in the case of the low H_2 partial pressure, that in Flibe is too low to promote process (2). When process (2) becomes a slow

Table 1
HT and TF rate in released tritium at steady-state

H_2 partial pressure in purge gas [Pa]	HT rate in tritium release [%]	TF rate in tritium release [%]
100 000	100	0
10 000	100	0
1000	100	0
100	17	83
10	7.4	93
1	0.9	99

Table 2
Concentrations of HT and H_2 in Flibe at steady-state

H_2 partial pressure in purge gas [Pa]	HT concentration in Flibe [mol/m^3]	H_2 concentration in Flibe [mol/m^3]
100 000	4.9×10^{-5}	5.0×10^{-2}
10 000	4.9×10^{-5}	5.0×10^{-3}
1000	4.9×10^{-5}	4.5×10^{-4}
100	8.2×10^{-6}	4.2×10^{-5}
10	3.6×10^{-6}	1.4×10^{-6}
1	4.4×10^{-7}	6.0×10^{-8}

process and the rate of HT production is limited, the T^+ concentration in Flibe at the steady-state would become very large to be sufficient to release TF with a very low mass transfer coefficient.

Because the inventory of TF in Flibe would be very large and the corrosion for the structural material by TF might be severe, to recover only HT is considered to be a candidate for tritium recovery from Flibe in an actual blanket system. In our experimental system, about 1.3×10^{-12} mol/s of tritium are generated and HT is released to the gas phase (H_2 is dissolved to the liquid phase) through 26.4 cm^2 of the surface area, while in an actual D–T blanket to generate 1 GWe, about 2×10^{-3} mol/s of tritium should be recovered. In order to recover only HT in an actual blanket, at least 4×10^4 m^2 of the surface area contacting with 1 atm of H_2 is required. Therefore, the contact area of Flibe with gas phase should be increased by some methods, such as, the spray tower methods, in which liquid Flibe is dispersed into submillimeter droplets (of much smaller size than the thickness of a Flibe liquid film); many small droplets of liquid Flibe could have a large total surface area of the order of 10^5 m^2.

4. Conclusion

For the tritium release from Flibe (Li_2BeF_4) a potential liquid tritium breeding material, three tritium transfer processes were considered: Process (1) is the direct release of generated T^+ to the purge gas as TF, process (2) is the conversion from T^+ to HT, and process (3) is the release of HT to the purge gas. The tritium release experiment was performed, focusing on the rate of the change of the tritium chemical species in Flibe. The temporal change of HT release rate has a dependence on the H_2 partial pressure in the system in the case of low H_2 partial pressure, while no dependence on H_2 partial pressure in the case of high H_2 partial pressure. The concentrations of four kinds of species T^+, HT, H_2 and H^+ dissolved in Flibe control the rate of the change of the tritium chemical species. At the steady-state in the case of low H_2 partial pressure, TF becomes the main chemical form of released tritium by decreasing rate of the tritium chemical change, which is caused mainly by the decrease of H_2 concentration in Flibe. This decrease of H_2 concentration is considered to be more large in an actual blanket, and the surface area of Flibe contacting with H_2 gas need to be greatly increased.

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