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Tritium release from neutron-irradiated Li_2O sintered pellets: isothermal annealing of tritium traps

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Abstract

Tritium release rate from Li_2O (71–86% T.D.) is found to follow the stretched exponential form, $dF/dt = \exp(-(t/\tau))^{\beta}$. The values of β are about 0.8 near 500 K and about 0.5 near 580 K. The activation energy of tritium release is calculated as approximately 92 kJ/mol at 493–533 K and 139 kJ/mol at 543–583 K. It is suggested that the rate controlling process of tritium release is detrapping from the irradiation defects that serve as trapping sites for tritium, and the recovery behavior of such irradiation defects significantly affects the tritium release behavior. No porosity dependence of tritium release was observed for these densities of Li_2O.

1. Introduction

Li_2O is one of the principal candidates for tritium breeding material in a fusion reactor. It is known that, in an operating fusion reactor, the irradiation defects in the breeding materials will be generated by fast neutrons, energetic tritons (2.7 MeV) and helium ions (2.1 MeV) generated in $^6Li(n,a)^3H$ reaction. It has been reported that such irradiation defects affect the tritium release and tritium inventory in the breeding materials [1–15]. In the previous studies, the behavior of the irradiation defects in Li_2O such as F^+ centers and Li colloidal centers and the interaction between such defects and tritium generated with irradiation in Li_2O have been studied with ESR, optical absorption, and other techniques.

It was established that tritium diffusivity in Li_2O is degraded by fast neutron irradiation below 1060 K, using the measurement of tritium diffusivity in Li_2O sample irradiated in FFTF [16]. For the Li_2O with sample density of 71–86% T.D., the defects recovery processes control the tritium release rate due to tritium trapping and detrapping in the defects [17]. It was also shown that the tritium release rate had no dependence on porosity within the density range 71–86% T.D., however, with Li_2O density over 87% T.D., the tritium release does depend strongly on porosity [18].

In this study, isothermal tritium release experiments were performed with Li_2O samples of 71%, 76%, 81% and 86% T.D. to clarify the relation between tritium release and defect recovery.

2. Experimental

The specimens were sintered Li_2O pellets of 71%, 76%, 81% and 86% T.D. The preparation of the pellets has been described in detail elsewhere [19]. The 99% pure Li_2O powder prepared by Cerac Co. was heated in vacuum at 970 K for 4 h to decompose Li_2CO_3 and LiOH. After the heat treatment, the powder was pressed without binder in the pressure range of 9.8×10^7–4.9×10^8 Pa followed by sintering for 2–4 h in a vacuum in the temperature range 1370–1570 K.

Small pieces ($2 \times 2 \times 2$ mm^3) were cut from Li_2O sintered pellets and heated in vacuum at 970 K for 4 h.

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After heat treatment, the specimens were enclosed in quartz ampoules with helium at about 1/3 atmospheric pressure, and irradiated with thermal neutrons to fluence up to 4×10^{16} n/cm^2 in the JRR-4 reactor at JAERI.

After irradiation, in order to heat the specimens up to the desired temperature as quickly as possible, the isothermal annealing was carried out in the following manner.

A platinum crucible containing specimens was temporarily held in a silicon rubber tube with a clamp. After the desired temperature of the furnace was attained, the crucible dropped into the furnace. Tritium released from the specimens in a flow (180 cm^3/min) of ammonia (NH_3) sweep gas at atmospheric pressure during isothermal annealing was measured with a proportional counter. By using an ammonia sweep gas, the adsorption of HTO on Li_2O surfaces and the production of LiOT is prevented. In addition, the adsorption of HTO on the inner walls of the piping and counter is precluded and this reduces the background level. The proportional counter was kept at about 400 K to suppress contamination by adsorption of tritium.

3. Results and discussions

3.1. Irradiation defect recovery and tritium release behavior

In the previous study [17,18], during a temperature ramp of 2 K/min, the tritium released from a Li_2O sample of 81% T.D. began at about 440 K, and the temperature of the release peak was about 570 K as shown in Fig. 1.

Fig. 1 also shows the recovery behavior of F^+ and Li colloidal centers, and the temperature dependence of the chemical form of tritium in Li_2O [6]. The results of experiments using ESR in Li_2O sintered pellets irradiated with neutron of 4×10^{16}–2×10^{17} n/cm^2 shows that the recovery of F^+ center depends on the neutron fluence. The recovery begins at about 420 and 440 K, and ends at about 570 and 630 K for the fluence of 4×10^{16} and 2×10^{17} n/cm^2, respectively [7]. The recovery beginning temperature of 440 K with the sample irradiated to 2×10^{17} n/cm^2 corresponds to the tritium release beginning temperature as shown in Fig. 1. The results of an in situ luminescence experiment with electron beam shows that the Li colloidal centers were generated by irradiation, and the disappearance of the centers begins at about 300 K and ends at about 630 K [12,14]. T^- in the irradiated Li_2O begins to transfer to T^+ at about 440 K, which is the temperature at which tritium release begins, and at about 570 K, the temperature of the tritium release peak, the conversion from T^- to T^+ is almost completed. These results show that generation and recovery of the irradiation defects such as F^+ and Li colloidal centers affects the tritium release behavior and the chemical form of tritium.

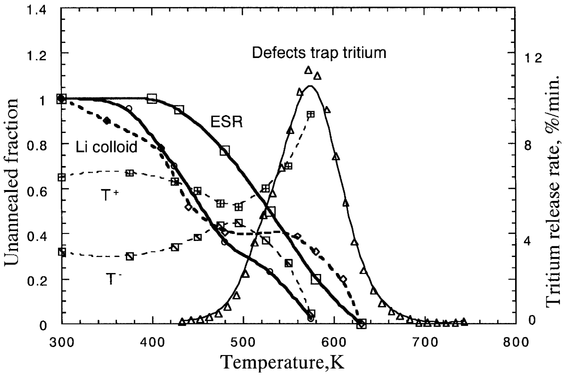

Fig. 1. Comparison of the change in T^+ and T^- abundances [6] with the annihilation of ESR signals of F^+ centers [7] and colloidal Li [14] in Li_2O during isochronal annealing.

3.2. Isothermal release experiment

Fig. 2 shows the time dependence of a typical tritium release from 71% T.D. Li_2O pellet with isothermal annealing. The release rate dF/dt is expressed using the Kohlrausch stretched exponential form as below,

$$dF/dt = \exp(-(t/\tau))^{\beta}, \quad (1)$$

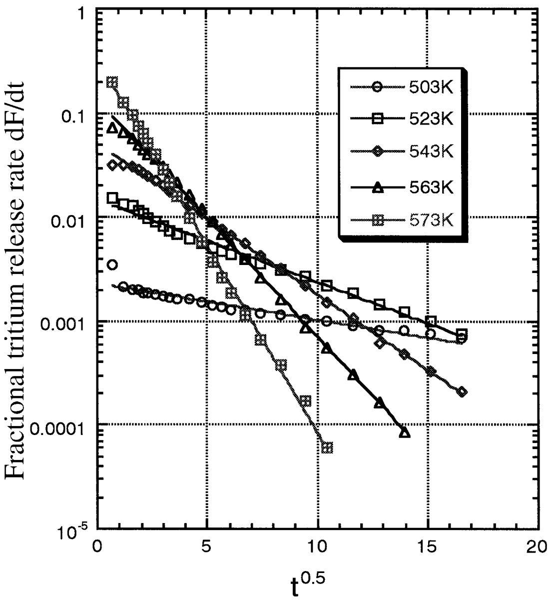

Fig. 2. Release rate dF/dt is expressed by Kohlrausch stretched exponential function $dF/dt = \exp(-(t/\tau))^{\beta}$.

where F is fraction released, t is time, τ is trap survival time and β is the stretched exponent. It was reported that the recovery behavior of many kinds of irradiation defects can be expressed by the Kohlrausch stretched exponential form [20–22]. Therefore, It is suggested that the tritium release behavior from Li_2O is affected by the recovery behavior of irradiation defects.

3.3. Analysis of release behavior with fractional release

As shown in Fig. 2, β is nearly equal to 0.5 at higher temperature. To estimate the value of β and τ at lower temperature, the time dependence of F is analyzed by JMKA method [23,24]:

$$\log(-\log(1-F)) = \log(b) + S\log(t). \qquad (2)$$

Fig. 3 shows the time dependence of $\log(-\log(1-F))$.

The value of β can be calculated using the slope and intercept shown in Fig. 3. Fig. 4 shows the temperature dependence of β for several different density samples. It shows that β has no dependence on porosity. It also shows that the value of β decreases with increasing in temperature, from about 0.8 at 495 K to about 0.5 at 583 K. These results suggest that the tritium release mechanism from Li_2O is affected by the chemical form change and the recovery of irradiation defects so that the fractional release rate cannot be expressed as a simple exponential form.

τ can be calculated by using intercept (b) shown in Fig. 3. Fig. 5 shows the temperature dependence of τ for the different density samples. τ is dependent on the release temperature, but not on porosity. This suggests that the condition of tritium traps change with the increase in temperature.

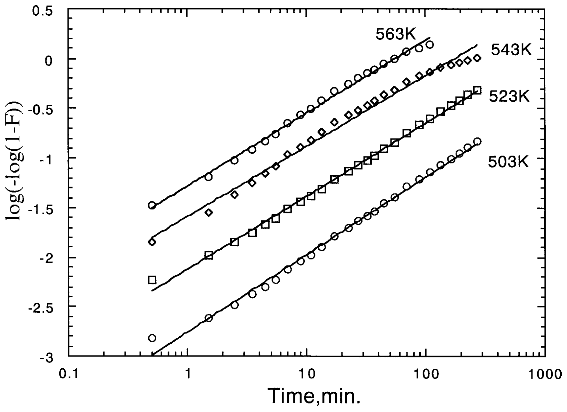

Fig. 3. Plot of $\log(-\log(1-F))$ as a function of log(time). The slope and intercept yield stretched exponent β and trap survival time τ, respectively.

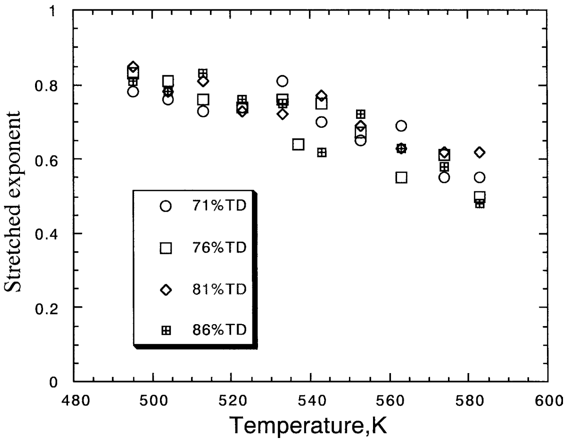

Fig. 4. Temperature dependence of the stretched exponent β for 71%, 76%, 81% and 86% T.D.

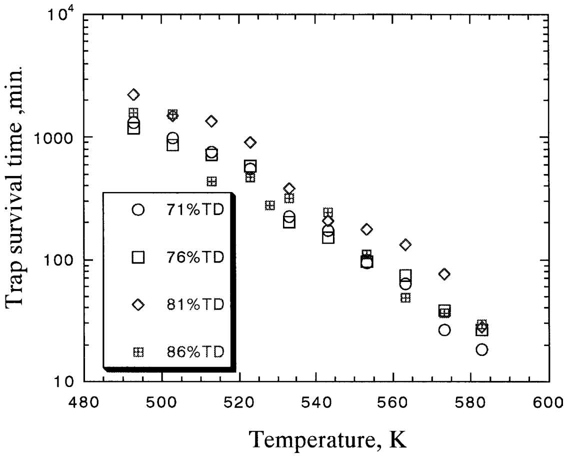

Fig. 5. Temperature dependence of the trap survival time τ for 71%, 76%, 81% and 86% T.D.

3.4. Analysis of the activation energy

The Arrhenius plots of τ are given in Fig. 6. The value of τ is calculated to be 92 kJ/mol in the lower temperature range, and 139 kJ/mol at higher temperatures. The temperature dependence of τ is believed to follow a simple activation process, but there are at least two different activation processes.

As shown in Fig. 1, the ratio of T^- of tritium in Li_2O increase with temperature in the range 380–500 K, and rapidly decreases with temperature in the range 500–600 K. This would be related to the recovery behavior of Li colloidal centers [12,14]. It suggests the presence of an interaction between Li colloidal center and T^- to form Li–T. In the lower temperature region (440–520 K), it is believed that T^- in Li–T is detrapped by the

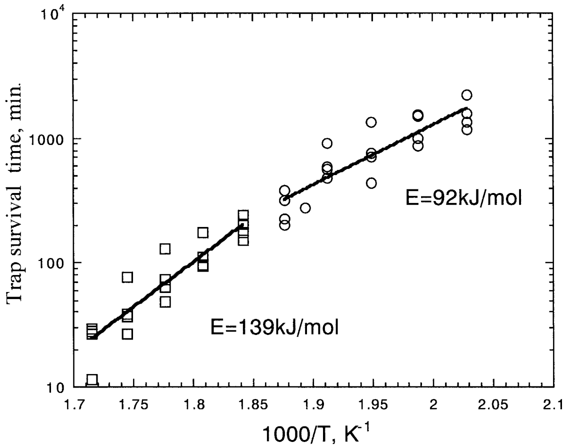

Fig. 6. Arrhenius plots of the trap survival time τ.

disappearance of the Li colloidal centers, and released with a lower activation energy of 92 kJ/mol.

F^+ centers and O^{2-} ions are generated via a reaction of F^0 center and O^- ions in the temperature region higher than 500 K. The ratio of T^+ in Li_2O increases rapidly with increase in temperature and becomes nearly 1 at 590 K. It was observed by ESR that the temperature where F^+ centers disappears is almost coincident with the temperature where T^+ begins to increase. It suggests that there is some relation between the disappearance of F^+ centers and change in the chemical form of tritium.

In the higher temperature region, almost all tritium would exist as T^+, reacts with O^{2-} ions, and finally is released as T^+ which is the stable chemical form. This is probably the reason why the activation energy of tritium release becomes larger, about 140 kJ, in the higher temperature region.

4. Conclusions

The tritium release rate from Li_2O (71–86% T.D.) is found to follow the stretched exponential form, $dF/dt = \exp(-(t/\tau))^{\beta}$. The values of β are about 0.8 near 500 K and about 0.5 near 580 K. The activation energy of tritium release is calculated approximately as 92 kJ/mol at 493–533 K and 139 KJ/mol at 543–583 K. It is suggested that the rate controlling process of tritium release is detrapping from the irradiation defects that serve as trapping sites for tritium, and the recovery behavior of such irradiation defects significantly affects the tritium release behavior. No porosity dependence of tritium release was observed in this density range.

Tritium release mechanisms from porous sintered Li_2O is complicated and strongly depends on porosity and neutron fluence. Generation and disappearance of the irradiation defects produced by energetic neutron radiation has an important roll in durability of the breeding materials and characteristics of tritium release. The porosity and neutron fluence dependence of tritium release should be clarified by isothermal experiments in planned further studies.

References

[1] K. Uchida, K. Noda, T. Tanifuji, S. Nasu, T. Kirihara, A. Kikuchi, Phys. Status solidi A 58 (1980) 557.
[2] K. Noda, K. Uchida, T. Tanifuji, S. Nasu, J. Nucl. Mater. 91 (1980) 234.
[3] K. Noda, K. Uchida, T. Tanifuji, S. Nasu, Phy. Rev. B 24 (1981) 3736.
[4] K. Noda, T. Tanifuji, Y. Ishii, H. Matsui, N. Masaki, S. Nasu, H. Watanabe, J. Nucl. Mater. 122&123 (1984) 908.
[5] H. Kudo, K. Okuno, J. Nucl. Mater. 133&134 (1985) 192.
[6] K. Okuno, H. Kudo, J. Nucl. Mater. 138 (1986) 31.
[7] K. Noda, Y. Ishii, H. Matsui, H. Watanabe, Radiat. Eff. Def. Solids 97 (1986) 297.
[8] H. Moriyama, J. Oishi, K. Kawamura, J. Nucl. Mater. 161 (1989) 197.
[9] N.M. Masaki, K. Noda, H. Watanabe, R.G. Clemmer, G.W. Hollenberg, J. Nucl. Mater. 212–215 (1994) 908.
[10] P. Vajda, F. Beuneu, Phys. Rev. B 53 (1996) 5335.
[11] F. Beuneu, P. Vajda, Phys. Rev. Lett. 76 (1996) 4544.
[12] P. Vajda, F. Beuneu, J. Nucl. Mater. 258–263 (1998) 495.
[13] F. Beuneu, P. Vajda, Radiat. Eff. Def. Solids 150 (1999) 141.
[14] V. Grismanov, S. Tanaka, J. Tiliks, G. Kizane, A. Supe, T. Yoneoka, Fus. Eng. Des. 39&40 (1998) 68.
[15] V. Grismanov, M. Taniguchi, S. Tanaka, T. Yoneoka, J. Nucl. Mater. 258–263 (1998) 537.
[16] T. Tanifuji, D. Yamaki, K. Noda, O.D. Slagle, F.D. Hobbs, G.W. Hollenberg, Fus. Thechnol. (1996) 1455.
[17] T. Tanifuji, D. Yamaki, S. Jitsukawa, J. Nucl. Mater. 307–311 (2002) 1456.
[18] T. Tanifuji, D. Yamaki, T. Takahashi, A. Iwamoto, J. Nucl. Mater. 283–287 (2000) 1419.
[19] T. Takahashi, T. Kikuchi, J. Nucl. Mater. 91 (1980) 93.
[20] J. Kakalios, R.A. Street, W.B. Jackson, Phys. Rev. Lett. 59 (1987) 1037.
[21] W.B. Jackson, J. Kaklios, Phys. Rev. B 37 (1988) 1020.
[22] D. Redfield, R.H. Bube, Appl. Phys. Lett. 54 (1989) 1037.
[23] H. Zhang, J.F. Banfifld, Am. Mineral. 84 (1999) 528.
[24] H. Binder, A. Anikin, B. Kohlstrunk, J. Phys. Chem. B 103 (1999) 450.