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Journal of Nuclear Materials 307–311 (2002) 1456–1460

journal of nuclear materials

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Tritium release from neutron-irradiated Li_2O sintered pellets: fluence dependence

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Abstract

The tritium release curves from the lower density region (71–86% TD) sintered pellets which were irradiated by thermal neutrons up to the fluences of 4×10^{20}, 2×10^{21}, 2×10^{22} and 2×10^{23} n/m^2 have one peak around 570, 590, 610 and 620 K, respectively. It means that no dependence on porosity is observed for these densities and fluences. This suggests that the tritium generated by thermal neutron irradiation is trapped in the irradiation defects introduced by irradiation of the bulk. The curves from the intermediate density region (87–89% TD) pellets which were irradiated up to same fluences as the lower also have one peak around 620, 640, 660 and 680 K, respectively. This means that the peaks tend to shift to higher temperatures by thermal neutron fluence, much the same as the 71–86% TD pellets. The curves from the higher density region (90–92.5% TD) pellets irradiated up to 4×10^{20} n/m^2 have plural peaks. The curves from the pellets irradiated up to 2×10^{21}, 2×10^{22} and 2×10^{23} n/m^2 also have the same number of peaks, and a dependence of the temperatures of the peaks on the fluences is not observed.

1. Introduction

Li_2O is one of the principal candidates for tritium breeding materials in the fusion reactor system. In the solid breeding materials, various kinds of irradiation defects are produced by exposing to high energy radiations during the fusion reactor operations. These irradiation defects are considered to affect the tritium release behavior from and the tritium inventory in the solid breeding materials. Many researchers have investigated the production and reduction behavior of the point defects in Li_2O such as F^+ center and Li colloid, and effects of the defects on tritium release behavior from Li_2O by using methods of ESR, optical absorption and so on [1–15].

In the previous study, the tritium release behavior from Li_2O single crystal was investigated to estimate the tritium diffusion coefficient in the bulk [16]. The irradiation effects of fast neutrons on the diffusion coefficient were also investigated by using the FFTF and it was clarified that the fast neutron irradiation degrades the coefficient below the temperature of 1060 K [17]. In addition, the tritium release behavior from Li_2O sintered pellets of various densities (71–98.5% TD) was investigated by constant heating rate tests. It was clarified that there is a porosity dependence of the tritium release rate in the density range over 87% TD, while no dependence is observed in the density range under 86% TD, and that the tritium release process consists of three different stages [18]. From the investigation of the helium release behavior from sintered and single-crystal Li_2O, it was clarified that the temperature of the peak in the helium release curves in the constant heating rate tests shifts to higher temperature with increase with the neutron fluence [19,20]. These results suggest that the effects of irradiation defects are considered to affect the tritium and helium behavior in Li_2O significantly.

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0022-3115/02/$ - see front matter
PII: S0022-3115(02)01285-0

In the present study, the neutron fluence dependence on the tritium release behavior from sintered Li_2O with various bulk density (71–92.5%) was investigated. Various fluences of thermal neutron irradiation (4×10^{20}–2×10^{23} n/m^2) were performed to investigate the effects of irradiation defects on the tritium release behavior.

2. Experimental

Small pieces of sintered Li_2O ($2 \times 2 \times 2$ mm^3) with various bulk densities (71–92.5% TD) which were cut from the pellets (12 mm $\varnothing \times 10$ mm L) were used as specimens. The preparation method and characterization of the pellets were reported elsewhere [21]. The starting material is 99% pure Li_2O powder by CERAC Co. The powder was heated at 970 K for 4 h in vacuum to decompose Li_2CO_3 and LiOH. After the heat treatment, the powder was pressed under pressure of 9.8×10^7–4.9×10^8 Pa without binder and sintered in vacuum for 2–4 h in the temperature range of 1370–1570 K. In the density range over 86% TD, the closed porosity in the pellets rapidly increases with increase of the density and reaches maximum at 90% TD The grain size of the sintered pellets is from about 9.5 μm at 71% TD to about 35 μm at 92.5% TD.

The specimens are sealed up in quartz ampoules with He gas (4×10^5 Pa) after heated at 970 K for 4 h in vacuum. The irradiation specimens were not affected by the moisture in the atmosphere because they were sealed up in the quartz ampoules with He. In addition, He gas has an excellent thermal conductivity. Irradiation was performed in the cooled water (about 320 K) in the reactor. The ampoules directly contact with the cooled water. Therefore, the estimated temperature in the quartz ampoules is below about 340 K. The specimens were irradiated up to 4×10^{20}, 2×10^{21}, 2×10^{22} and 2×10^{23} n/m^2 with thermal neutrons in JRR-2 (flux level 4×10^{17} n/m^2 s) and JRR-4 (flux level 3×10^{17} n/m^2 s). In the thermal neutron fluence region of this experiment, the total Li burn-up is considered to be proportional to the thermal neutron fluence. The calculated total Li burn-up is 0.0003% and 0.15% for the thermal neutron fluence of 4×10^{20} and 2×10^{23} n/m^2, respectively.

After irradiation, the tritium release from the samples was measured with a proportional counter in a flow (180 cm^3/min) of ammonia sweep gas (NH_3) at atmospheric pressure during a constant heating rate of 2 K/min. By using ammonia sweep gas, HTO adsorption on the Li_2O surface and production of LiOT were prevented, and HTO adsorption on the inner wall of the piping and the counter is also prevented to reduce the background level of tritium. In the measuring system, the counter was kept at about 400 K to suppress the contamination of the counter due to adsorption of tritium [16].

3. Results and discussion

3.1. Neutron fluence dependence

3.1.1. Lower density region (71–86% TD)

Fig. 1 shows the tritium release rate from sintered Li_2O with 71–81% and 86% TD in the constant heating rate (2 K/min) tests. It is shown that the temperature of the tritium release peak shifts to higher temperatures with increase of the neutron fluence (Li burn-up), that is, 570 K for 4×10^{20} n/m^2, 590 K for 2×10^{21} n/m^2, 610 K for 2×10^{22} n/m^2 and 620 K for 2×10^{23} n/m^2 in the lower density region (71–86% TD). This means the tritium release behavior depends on the neutron fluence significantly and suggests that tritium trapping in irradiation-induced defects plays an important role in the tritium release behavior.

3.1.2. Intermediate density region (87–89% TD)

Fig. 2 shows the tritium release rate from sintered Li_2O with 87%, 88% and 89% TD in the constant heating rate (2 K/min) tests. It is shown that the temperature of the tritium release peak shifts to higher temperatures with the increase of neutron fluence, that is, 620 K for 4×10^{20} n/m^2, 640 K for 2×10^{21} n/m^2,

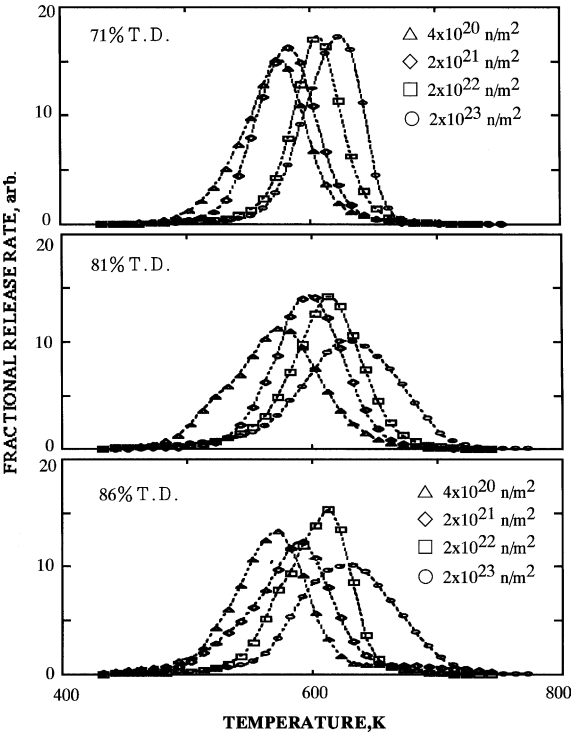

Fig. 1. Fluence dependence for tritium release rate from sintered Li_2O pellets of 71–86% TD during a temperature ramp of 2 K/min.

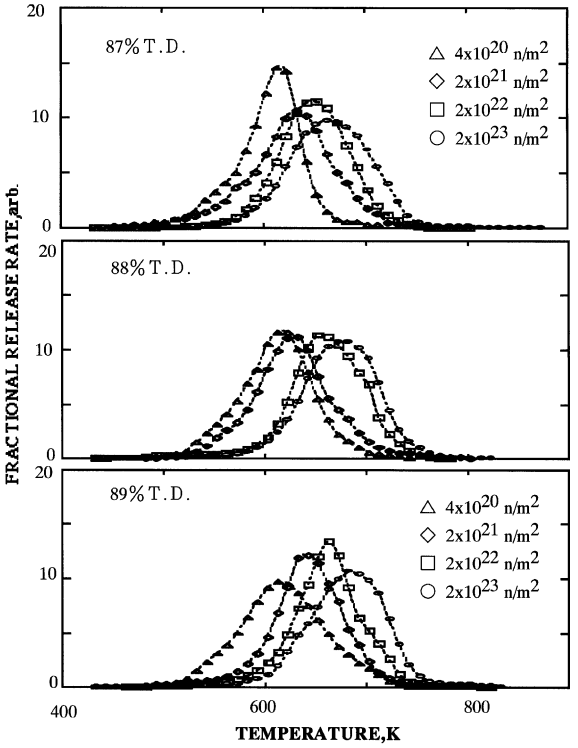

Fig. 2. Fluence dependence for tritium release rate from sintered Li_2O pellets of 87–89% TD during a temperature ramp of 2 K/min.

660 K for 2×10^{22} n/m^2 and 680 K for 2×10^{23} n/m^2. From the comparison between Figs. 1 and 2, it is found that the temperature of the peaks in the intermediate density region (87–89% TD) is 50 K higher than that in the lower range (71–86% TD) for the same neutron fluence and similar specimens (Fig. 3). This result suggests that the rate determining step in the intermediate region is different from that in the lower range.

In the lower density region (71–86% TD), the open and closed porosity show 25% and 3.5% for 71% TD, and 11% and 3% for 86% TD, respectively, that is, the ratio of the closed to the open porosity is between 0.14 and 0.27. This large open to the closed porosity ratio is considered to be the small contribution of interconnected pores to the tritium release, and the cause of the constant temperature of the peak in this density region for same neutron fluence. In the intermediate density region (87–89% TD), the ratio of closed to open porosity is between 0.57 and 1.8. The difference of the temperature of the peaks between the lower and intermediate density region is considered to be caused by the change of the ratio of closed to open porosity. This suggests that the rate determining step of the tritium release in the intermediate density region is considered as the *advection* through the open pores via adsorption and desorption on the inner wall of the pores, or the diffusion in the gas phase in the interconnected pores [18].

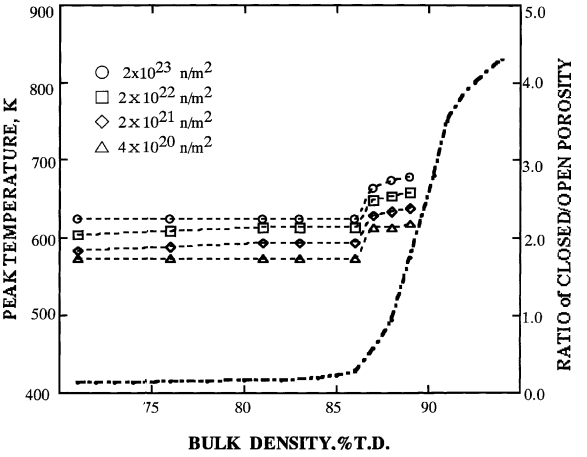

Fig. 3. Fluence and porosity dependence for tritium release peak temperature from sintered Li_2O pellets of 71–89% TD during a temperature ramp of 2 K/min.

A similar dependence on the neutron fluence was also observed in the helium release behavior. For helium release from sintered Li_2O, it is observed that the temperature of the peaks in the helium release curves shifts to higher temperatures (about 900–1100 K) with increase of neutron fluence [19]. For helium release from Li_2O single crystals, the temperature of the peaks in the helium release curves also shifts to higher temperatures (about 1200–1500 K) with increase of neutron fluence [20]. These results suggest that there are some helium bubbles and hole–helium aggregation defects which are able to exist at these high temperatures, and they become the trapping sites of helium produced in bulk Li_2O by neutron irradiation.

3.1.3. Higher density region (90.5–92.5% TD)

Fig. 4 shows the tritium release rate from sintered Li_2O with 90.5% and 92.5% TD in the constant heating rate (2 K/min) tests. It is shown that the temperature of the tritium release peak is independent on the neutron fluence. There are two peaks around 650 and 750 K in the tritium release curves from 90.5% TD specimens, and three peaks around 650, 800 and 1000 K in the curves from 92.5% TD specimens. This result suggests that the main tritium release mechanism in this density region is the release of the tritium trapped in the closed pore because the closed porosity is too high in this region.

3.2. Irradiation defects recovery and tritium release

Fig. 5 shows the recovery behavior of F^+ centers produced in sintered Li_2O by oxygen ion irradiation and

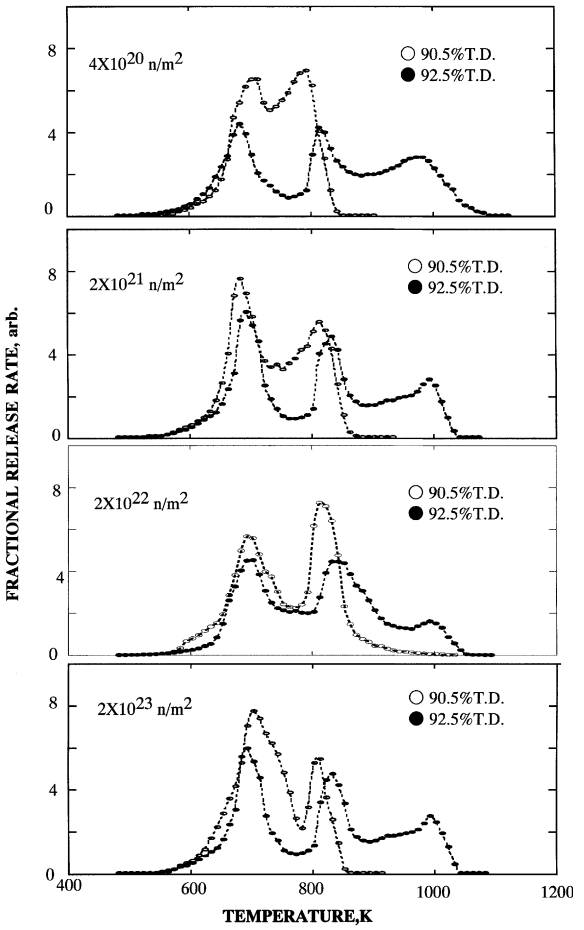

Fig. 4. Fluence dependence for tritium release rate from sintered Li_2O pellets of 90.5% TD and 92.5% TD forduring a temperature ramp of 2 K/min.

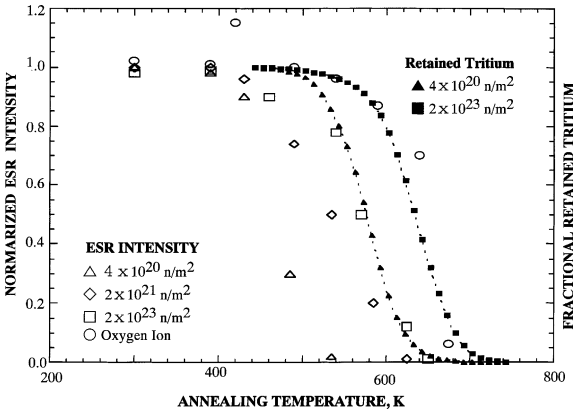

Fig. 5. Fluence dependence for the recovery of F^+ center produced in sintered Li_2O irradiated with oxygen ion and thermal neutron observed by ESR and the amount of retained tritium in 81% TD sintered Li_2O.

neutron irradiation up to 4×10^{20}, 2×10^{21} and 2×10^{23} n/m^2 observed by the ESR method. As shown in this figure, the recovery behavior of F^+ center depends on the neutron fluence, that is, the recovery temperatures are about 420–520 K for 4×10^{20} n/m^2, 460–620 K for 2×10^{21} n/m^2 and 470–650 K for 2×10^{23} n/m^2 [3,4]. The recovery temperature for the oxygen ion irradiation is about 520–670 K which is higher than that for the neutron irradiation [7]. The similar result of the recovery temperature of F^+ centers in sintered Li_2O is also observed by the optical absorption method by Uchida et al. [1]. The irradiation temperature and neutron flux level in the ESR and opitical adsorption experiments were similar to this experiment. The concentration of the irradiation defects increases with the increase of the neutron fluence, it suggest that recovery temperature of the defects and the peaks in the tritium release curve do not depend on neutron flux.

Fig. 5 also shows the amount of retained tritium in 81% TD sintered Li_2O in the constant rate heating tests for the neutron fluence of 4×10^{20} and 2×10^{23} n/m^2. As shown in this figure, the temperature of tritium release for 2×10^{23} n/m^2 is higher than that for 4×10^{20} n/m^2. The temperature of tritium release is higher by approximately 60–90 K than that of F^+ center recovery for the same neutron fluence. As reported in the previous paper [11], the apparent activation energy of tritium release from 81% TD sintered Li_2O is found to be 129 kJ/mol, which is almost equal to that of F^+ center recovery, 135 kJ/mol, reported by Noda et al. [3]. These results suggest that the tritium release behavior from 81% TD sintered Li_2O is significantly effected by F^+ center recovery behavior.

F^+ centers produced by neutron irradiation are considered to aggregate and produce F-aggregate centers by increase of the neutron fluence. F-aggregate centers are extinguished by the move of adjacent interstitial oxygen atoms and produce Li colloidal metal by increase of the annealing temperature. Colloidal Li metal is also produced by electron or gamma irradiation. It is considered that colloidal Li metal interacts with tritium and traps it by producing Li–T bonds [14]. However, the temperature of colloidal Li metal recovery is around 720–900 K [15] which is much higher than that of tritium release. It is not depicted that the tritium trapping by colloidal Li metal is the rate determining step of tritium release from 81% TD sintered Li_2O.

Colloidal Li metal was also observed by the ESR method in single-crystal Li_2O irradiated by fast neutron in the FFTF up to the fluence of 3.9×10^{26} n/m^2 [9]. From the tritium release experiment using the FFTF specimen, it is found that the tritium diffusion coefficient degrades below the temperature of 1060 K, compared with the results from the experiment using the JRR-4 specimen [17]. This result suggests that there are some aggregations of irradiation defects such as dislocation

loops which are able to exist even at 1060 K in the FFTF specimen. However, because the temperature of the recovery of the such defects is much higher than that of tritium release, these kind of defects is not considered to affect the tritium release behavior from 81% TD sintered pellets irradiated in JRR-4.

4. Conclusion

The tritium release behavior from Li_2O sintered pellets with various densities (71–92.5% TD) is investigated by the constant heating rate tests. It is clarified that there is a porosity dependence of the tritium release rate in the density range over 87% TD, while no dependence is observed in the density range under 86% TD, and there is a neutron fluence dependence of the tritium release rate in the density range under 89% TD, while no dependence is observed in the density range over 90.5% TD. From these results, it is considered that the rate determining step of the tritium release changes with the density change, described as follows: (1) lower density region (71–86% TD): the detrapping of tritium trapped in the point defects due to the recovery of the defects; (2) intermediate density region (87–89% TD): the migration through the interconnected pores via adsorption and desorption on the inner wall of the interconnected pores, and the diffusion in the gas phase in the interconnected pores; (3) higher density region (90.5–92.5% TD): the detrapping of tritium trapped in the closed pores.

It is clarified that the tritium release process from sintered pellets consists of many elemental mechanisms and is significantly affected by porosity and neutron fluence. The production and reduction of irradiation defects under high energy radiation such as neutrons are considered to play an important role in the assessment of stability and tritium release characteristics of solid breeding materials.

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. 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] R. Shah, A. De Vita, M.C. Payne, J. Phys.: Condensed Matter 7 (1995) 6981.
[11] P. Vajda, F. Beuneu, Phys. Rev. B 53 (1996) 5335.
[12] F. Beuneu, P. Vajda, Phys. Rev. Lett. 76 (1996) 4544.
[13] P. Vajda, F. Beuneu, J. Nucl. Mater. 258–263 (1998) 495.
[14] V. Grismanov, S. Tanaka, J. Tiliks, G. Kizane, A. Supe, T. Yoneoka, Fusion 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, K. Noda, T. Takahashi, H. Watanabe, J. Nucl. Mater. 149 (1987) 227.
[17] T. Tanifuji, D. Yamaki, K. Noda, O.D. Slagle, F.D. Hobbs, G.W. Hollenberg, Fusion Technol. (1996) 1455.
[18] T. Tanifuji, D. Yamaki, T. Takahashi, A. Iwamoto, J. Nucl. Mater. 283–287 (2000) 1419.
[19] T. Tanifuji, D. Yamaki, K. Noda, Fusion Eng. Des. 39–40 (1998) 723.
[20] D. Yamaki, T. Tanifuji, K. Noda, J. Nucl. Mater. 258–263 (1998) 549.
[21] T. Takahashi, T. Kikuchi, J. Nucl. Mater. 91 (1980) 93.