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Study on interaction of hydrogen isotopes with radiolysis products in lithium oxide

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Abstract

Out-of-pile tritium release experiments were performed for Li_2O polycrystalline powder (2–4 mm) irradiated by 2.2 MeV electrons to various absorbed doses up to 100 MGy and by thermal neutrons with a fluence of 10^{17} neutron/m^2. The linear temperature increase of the electron-irradiated samples showed two tritium release peaks: first started at around 600 K with a maximum at 800 K and second appeared at around 950 K with the maximum approximately at 1200 K. It is thought that the tritium release at high temperatures is due to the thermal decomposition of LiT. The formation of LiD under the electron irradiation was investigated by using the diffuse-reflectance Fourier transform infrared (FTIR) absorption spectroscopy. The Li_2O powder was irradiated by electron accelerator under D_2 containing atmosphere (N_2 +10% D_2). A Specific absorption band for the Li_2O sample was observed at 668 cm^{-1} and attributed to the Li–D stretching vibration. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Lithium oxide has been suggested as a suitable breeding blanket material for a fusion reactor. In an operating fusion reactor, the tritium breeding blanket should reach a steady-state condition whereby the tritium release rate equals the production rate. The tritium release must be fast enough so that the tritium inventory in the blanket does not become excessive. Slow tritium release will result in a large tritium inventory, which is unacceptable from the both economic and safety viewpoints.

The irradiation damage in Li_2O single crystals exposed to a high fluence with fast neutrons ($3.9 \cdot 10^{26}$ neutron/m^2) at about 650 K has been investigated by methods of electron spin resonance and optical absorption in the BEATRIX-II program [1]. The electron spin resonance data have been interpreted to indicate the presence of F-center aggregates in Li_2O single crystals with 1.8% and 0.07% ^6Li concentration. F-center aggregates are nothing more nor less than Li-atom aggregates which consist from the Li-atom ions surrounded by the F-centers [2]. The integral charge of such a cluster is negative. In most of the blanket designs using the Li_2O, the ^6Li enrichment of Li_2O is high (about 50–60%) and the neutron fluence at the lifetime is expected to be higher than that reached in the experiments performed by Noda et al. [1], and hence a high concentration of F-center aggregates could be created in the blanket. The operating temperatures for a typical blanket design using Li_2O are in the range of 720–920 K [3]. The F-center aggregates will remain in Li_2O in the lower temperature part of the blanket, since they are completely recovered at around 923 K [4]. This can cause a tritium inventory due to its trapping by Li-atom aggregates. Thus, the irradiation tests up to a high fluence at temperatures in the lower temperature part of the blanket are required.

The research on the influence of radiation defects on tritium release behavior from polycrystalline Li_2O [5] has revealed that the radiation defects in Li_2O cause the retention of tritium. It has been thought that the tritium recovery is affected by the formation of Li–T bond, which is tolerant of high temperatures; for instance, the thermal decomposition of Li–H bond is estimated at 1223 K [6]. The retardation of tritium decreased with increasing absorbed dose in the range from 50–140 MGy. In order to confirm the tritium retention observed

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in in-pile experiments [5], the out-of-pile tritium release measurements were performed in the present work. The experiments were carried out for the polycrystalline Li_2O powder heated up to 1273 K.

To evaluate the temperature efficient for the formation of Li–T bond the following simulation was carried out. The Li_2O powder was irradiated by an electron accelerator under D_2 containing atmosphere (N_2 +10% D_2) at various temperatures, and the formation of LiD was investigated by using the diffuse-reflectance FTIR absorption spectroscopy.

2. Experimental

The out-of-pile tritium release experiments were performed using a polycrystalline Li_2O of the particle size of 2–4 mm. The sample was 99.9% pure (Al: 0.02%, Ca: 0.05%, Cu: 0.001%, Fe: 0.01%, Si: 0.01%, Sn: 0.03%). The specimens were sealed in quartz containers filled with air atmosphere and irradiated by accelerated electrons (energy – 2.2 MeV, dose rate – 8 kGy/s, temperature – around 370 K) to absorbed dose up to 100 MGy at the DYNAMITRON facility of the University of Tokyo.

Afterwards, the specimens were exposed at about 310 K to the fluence of 10^{17} thermal neutron/m^2 at the research reactor “YAYOI” of the University of Tokyo. The samples without prior irradiation by electrons were exposed to the same fluence of thermal neutrons and used as reference samples. The out-of-pile tritium release experiments were carried out during the temperature transient from 293 to 1273 K. The temperature ramp was 10 K/min. The released tritium was removed by the sweep gas of N_2 and detected by the ionization chamber.

The formation of LiD under the electron irradiation was investigated by using diffuse-reflectance FTIR absorption spectroscopy. The Li_2O powder (48–65 mesh) was irradiated by electron accelerator under D_2 containing atmosphere (N_2 +10% D_2) at around 373, 673 and 893 K. For the reference sample we used the annealed Li_2O powder, which was examined by diffuse-reflectance FTIR absorption spectroscopy under Ar and Ar + D_2 atmospheres.

3. Results and discussion

3.1. Out-of pile tritium release

Fig. 1 shows the tritium release curve of the polycrystalline Li_2O specimen exposed at around 310 K to the fluence of 10^{17} thermal neutron/m^2. The sharp peak of released tritium can be seen at around 750 K. The experimental data indicate that there is no influence of radiation defects on tritium release. The absorbed dose for this specimen is estimated at around 10 kGy. Thus, the formation of simple F-centers proceeds at such low absorbed doses [5,7]. It seems likely that the interaction of F-centers with tritium at low irradiation dose is negligible.

The irradiation of Li_2O specimens by 2.2 MeV electrons to an absorbed dose of 75 MGy followed with the fluence of 10^{17} thermal neutron/m^2 causes the change of the tritium release kinetics (Fig. 2). One can recognize two broad peaks in the tritium release curve: the first

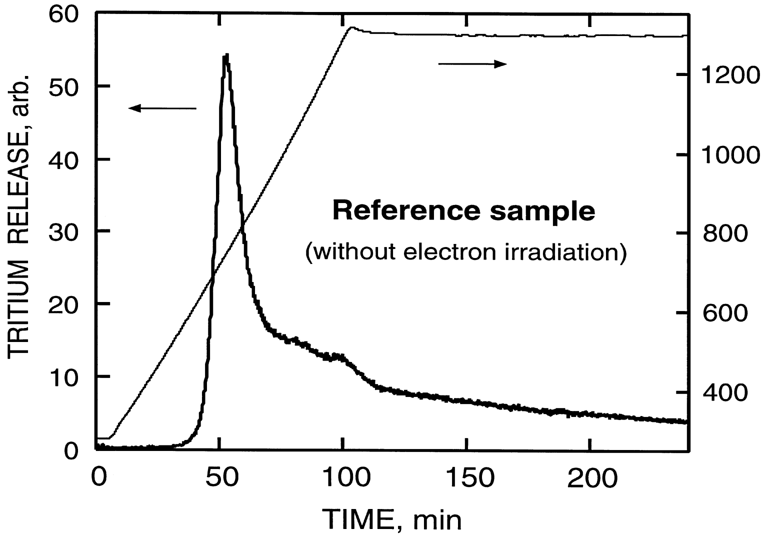

Fig. 1. Out-of-pile measurement of tritium release from the Li_2O specimen irradiated by thermal neutrons to the fluence of 10^{17} neutron/m^2.

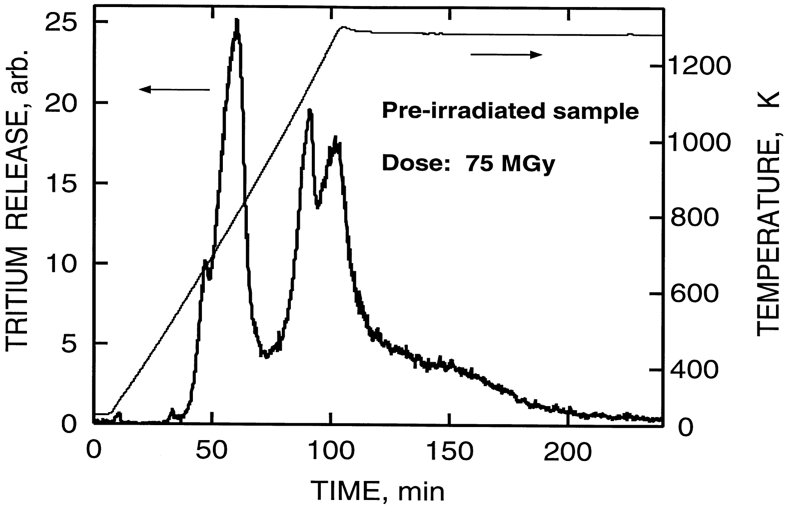

Fig. 2. Out-of-pile measurement of tritium release from the Li_2O specimen pre-irradiated by 2.2 MeV electrons to the absorbed dose of 75 MGy and by thermal neutrons to the fluence of 10^{17} neutron/m^2.

starts at 600 K with a maximum at 800 K and the second appears at 950 K with two maxima at 1150 and 1270 K. The first broad peak is associated with (1) desorption of physically and chemically adsorbed tritium on the sample surface, (2) decomposition of LiOT, and (3) migration of tritium dissolved in the bulk. It seems that the tritium bonded in the form of LiT is not released below 850 K as a significant fraction. The second peak begins to appear at around 950 K which is coincident with the phase transition of LiH (the 961.8 K corresponds to the crystal → liquid transition [8]). The second broad peak is thought to be due to the tritium bonded in Li–T bond, which was formed by the reaction of colloidal Li with tritium. The presence of the two maxima at about 1150 and 1270 K in this peak can be explained from the following viewpoint. The highest concentrations of radiation defects and tritium are in layers adjacent to the surface [9]. Thus, the first peak at 1150 K can be associated with tritium released due to the thermal decomposition of LiT at the near surface layers of the sample. Consequently, the second peak at 1270 K is the tritium released from the bulk of the sample where it was locally trapped at colloidal centers.

Very similar results were obtained in our preliminary investigation on the influence of radiation defects on tritium release from Li_2O single crystals [10]. The tritium release curve of the sample pre-irradiated with 2.2 MeV electrons to an absorbed dose of 50 MGy and followed by exposure to thermal neutrons with a fluence of 10^{17} n/m^2 consisted of a lot of small peaks, which were thought to be associated with tritium trapped by radiation defects at a different distance from the surface of the sample. One can suggest that the distribution of lithium particles created by irradiation is inhomogeneous. Because under irradiation the colloidal particles are formed by agglomeration of F-centers, the larger the colloids the larger is the cross section for the capture of new centers. This type of growth leads to a logarithmiconormal distribution of colloids size [11]. Such a distribution is determined by the grain size distribution or by the size distribution of cavities and dislocations created by irradiation [12]. This indicates an effective formation of colloidal particles in a certain region of matrix where cavities and dislocations are produced by irradiation. As a result, the tritium is locally trapped by lithium colloids in the form of LiT, which is thermally stable at high temperatures up to 950–1200 K. This effect is undesirable from the tritium inventory standpoint. However, the generation of tritium by thermal neutron irradiation was conducted at about 310 K, which is different from the operating temperature of the blanket of a fusion reactor.

In the paper by Vajda et al. [4], the recovery of metallic Li colloids and F^+ center agglomerates was reported to occur at around 673 and 923 K, respectively. F-center aggregates (in other words: clusters or agglomerates) are nothing more or less than Li-atom aggregates which consist of Li-atom ions surrounded by F-centers. Thus, in any case the formation of Li–T bond can occur in Li_2O even at high temperatures. The problem only is the amount of formed LiT. The concentration of F^+ center clusters determines the accumulation rate of LiT, and in its turn depends on temperature and irradiation dose. Thus, a certain region of temperature exists wherein the formation of Li–T bond is the most effective. In fact, the data of the ESR examination of Li_2O single crystals irradiated at 650 K by fast neutrons in the BEATRIX II [1] showed that the

F^+ center aggregates is created in Li_2O. According to our investigations [13], 650K can be a critical temperature for the formation of Li colloids. However, there is no clear understanding about the optimum temperature for the formation of F^+ center aggregates. Thus, the investigation of the influence of the radiolysis products on tritium release kinetics from Li_2O under the conditions expected in the thermonuclear reactor is desirable.

3.2. The observation of Li–D stretching vibration

In order to simulate the formation of Li–T bond under irradiation conditions, the following approach was applied. The Li_2O powder was exposed to accelerated electrons under N_2 +10% D_2 atmosphere at various temperatures. The absorbed dose was close to the range wherein the formation of colloidal Li can take place [13]. In that research, we found that the formation of colloidal Li in polycrystalline Li_2O under electron irradiation at 380 K occurred at an absorbed dose of about 100 MGy. It was presumed that the formed colloidal Li formed during electron irradiation reacted with D_2 absorbed in Li_2O powder to form the Li–D bond.

The samples prepared in the way described above were examined by using diffuse reflectance method of FTIR absorption spectroscopy. This method was successfully applied to the research on Li_2O surface nature [14,15]. Two absorption peaks of surface –OH groups were observed at 3677 and 3565 cm^{-1}, and three stretching vibration peaks of surface –OD groups were detected at 2748, 2717 and 2696 cm^{-1} [14]. The stretching vibration at 1218 cm^{-1} was attributed to Li–H bond [15].

Fig. 3 shows the absorption spectra of Li_2O irradiated by electrons to adsorbed dose of 100 MGy at about 373 K under N_2 +10% D_2 atmosphere. The stretching vibration peak can be seen at around 668 cm^{-1}. This peak is detected the first time for Li_2O, and it is attributable to the Li–D bond. The absorption peak at 668 cm^{-1} has been assigned to the Li–D bond due to two reasons: firstly, this peak appears in the FTIR spectra only under the D_2 containing atmosphere, and secondly, the shift to a lower wave number was observed for LiD in comparison with LiH. The latter observation is a common feature for the stretching vibration of chemical bonds with different hydrogen isotopes. For instance,

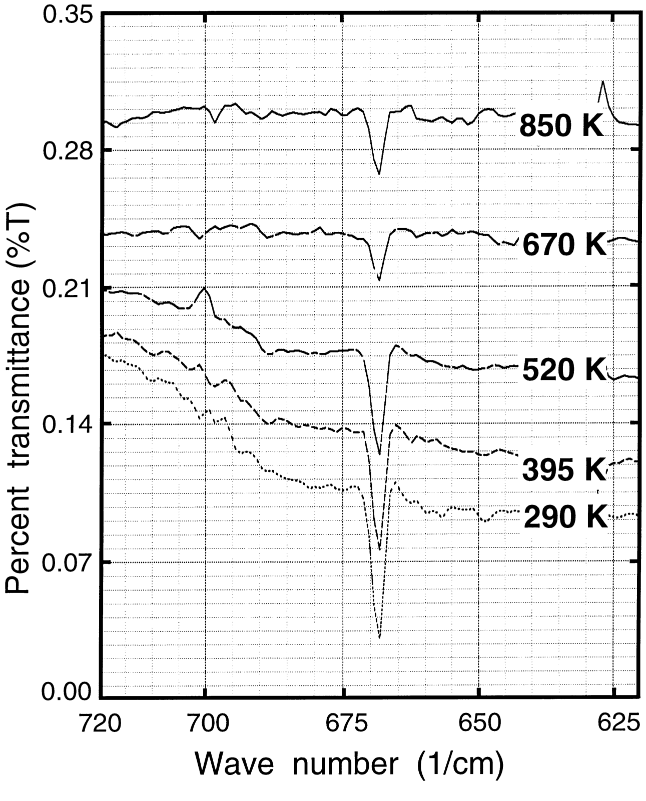

Fig. 3. Temperature dependence of absorption spectra of the Li_2O specimen irradiated at 373 K by 2.2 MeV electrons to the absorbed dose of 100 MGy under a N_2+10% D_2 atmosphere.

the absorption peaks for the pure LiH [15] and LiD [16] have been observed at 1280 cm and 880 cm^{-1}, respectively.

The intensity of the 668 cm^{-1} peak decreases with temperature up to 850 K (Fig. 3), but it reduces to almost the same value while the temperature was decreased. This fact indicates the thermal stability of the 668 cm^{-1} absorption peak. The irradiation of Li_2O powder by electrons at 673 and 893 K under N_2 + 10% D_2 atmosphere also resulted in the appearance of the stretching vibration peak at 668 cm^{-1}. However, the intensities of absorption peaks are lower than that detected for the sample irradiated at 373 K. In such a way, this testifies that the formation of Li–D bond is less efficient at high temperatures. The observed data suggest that the formation of Li–D bond can occur up to 893 K. However, a possibility of the production of Li–D bond at a higher temperature than 893 K is a subject to be studied.

The research on the FTIR absorption spectra of annealed Li_2O under Ar and Ar + D_2 atmospheres disclosed that the formation of Li–D bond occurs on the sample surface in the latter case. The absorption peak at 668 cm^{-1} observed for annealed Li_2O sample (Fig. 4) is coincident with that detected for irradiated by electron specimens under N_2 +10% D_2 atmosphere (Fig. 3). This fact does not allow us to conclude with confidence how the formation of Li–D bond proceeds in Li_2O during electron irradiation under atmosphere containing D_2: (1) due to the interaction with colloidal Li or (2) by reactions on the surface of Li_2O. It seems that the formation of Li–D bond easily takes place just in the presence of D_2 in the purge gas during the measurement of the diffuse-reflectance FTIR absorption spectrum.

4. Conclusions

It has been shown that the radiation defects introduced by electron irradiation cause the retention of tritium due to its bonding in the thermally stable state. The interaction of tritium with colloidal Li produced by electron irradiation is thought to result in the formation of Li–T bond. The tritium release at high temperatures (>950 K) indicates the decomposition of Li–T bond.

The formation of Li–D bond on the surface of Li_2O under the atmosphere containing D_2 was observed by diffuse-reflectance FTIR absorption spectroscopy for the

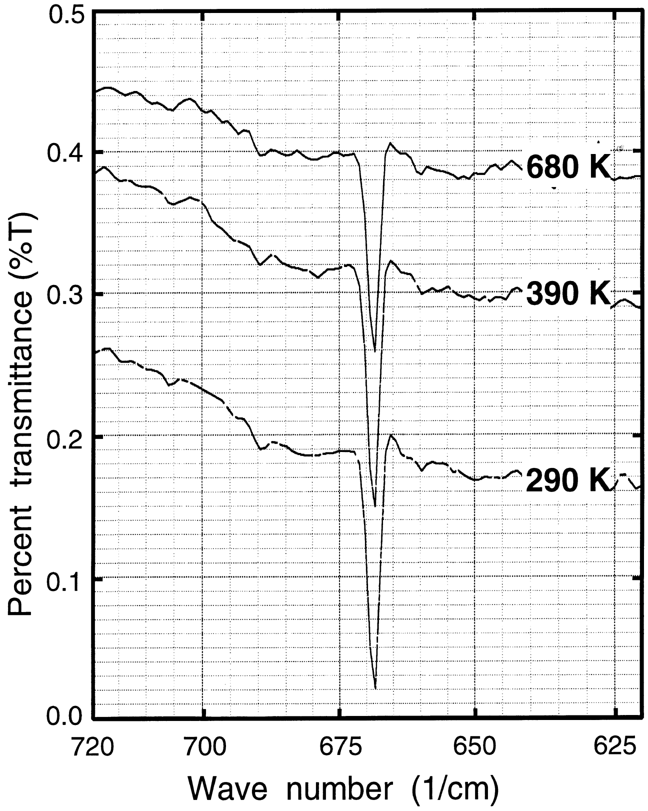

Fig. 4. Temperature dependence of absorption spectra of a non-irradiated Li_2O specimen under an Ar+D_2 atmosphere.

first time. However, a mechanism of the production of Li–D bond under electron irradiation in the presence of D_2 in the purge gas is unclear: the binding of D_2 in Li–D can proceed by surface reactions as well as by interaction of D_2 with colloidal Li produced by irradiation.

References

[1] N.M. Masaki, K. Noda, H. Watanabe, R.G. Clemmer, G.W. Hollenberg, J. Nucl. Mater. 212 (1994) 908.

[2] K. Schwartz, J. Ekmanis, Dielectric Materials: Radiation Processes and Radiation Stability, Zinatne, Riga, 1989 (in Russian).

[3] H. Takatsu, S. Mori, H. Yoshida, T. Hashimoto, T. Kurasawa, K. Koizumi, M. Enoeda, S. Satoh, T. Kuroda, T. Suzuki, K. Ioki, T. Kanazawa, in: Proceedings of SOFT-17, Roma, Italy, 1992, p. 1504.

[4] P. Vajda, F. Beuneu, these Proceedings.

[5] V. Grishmanov, S. Tanaka, J. Tiliks, G. Kizane, A. Supe, T. Yoneoka, Fusion Engrg. Design (in press).

[6] I. Barin, Thermodynamical Data for Pure Substances, VCH, New York, 1989.

[7] V. Grishmanov, S. Tanaka, J. Tiliks, in: Proceedings of SOFT-19, Lisbon, Portugal, 1996, p. 1451.

[8] M.W. Chase et al., J. Phys. Chem. Ref. Data (Suppl. 1) (1985) 1224-1227.

[9] A. Abramenkovs, J. Tiliks, G. Kizane, V. Grishmanov, A. Supe, J. Nucl. Mater. 248 (1997) 116.

[10] V. Grishmanov, S. Tanaka, T. Yoneoka, J. Nucl. Mater. 248 (1997) 128.

[11] A. Berthault, S. Bedere, J. Matricon, J. Phys. Chem. Solids 38 (1977) 913.

[12] R.T. Dehoff, Trans. Met. Soc. AIME 230 (1965) 25.

[13] V. Grishmanov, S. Tanaka, J. Tiliks, G. Kizane, A. Supe, L. Grigorjeva, Nucl. Instr. and Meth. Phys. Res. B 134 (1998) 27.

[14] S. Tanaka, M. Taniguchi, M. Nakatani, D. Yamaki, M. Yamawaki, J. Nucl. Mater. 218 (1995) 335.

[15] J.P. Kopazs, J. Ortiz-Villafuerte, C.E. Johnson, in: Proceedings of the Fourth Symposium on the Fabrication and Properties of Fusion Ceramics, 1995, p. 116.

[16] M.H. Brodsky, E. Burstein, J. Phys. Chem. Solids 28 (1965) 1655.