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Correlation between tritium release and thermal annealing of irradiation damage in neutron-irradiated Li_2SiO_3

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Abstract

Annihilation of irradiation defects and tritium release processes in the neutron-irradiated Li_2SiO_3 and Li_4SiO_4 were investigated by means of electron spin resonance and thermal desorption spectroscopy, respectively. The experimental results indicated that tritium release from both samples began just before the irradiation defects were completely annihilated. The isothermal annealing experiments for both samples showed that there were fast and slow annihilation processes of the defects with activation energies of 0.12 and 0.63 eV for Li_2SiO_3, and 0.12 and 0.56 eV for Li_4SiO_4. The fast annihilation process could result mainly from diffusion of trapped electrons into the defects, whereas the slow annihilation process could be attributed to the annihilation of E′-center by recovering oxygen ions (O^-). Therefore, the annihilation of E′-center would trigger the tritium release. A model of annihilation of E′-center and tritium behavior in neutron-irradiated ceramic tritium breeding materials is also proposed.

1. Introduction

Blanket systems for D–T fusion reactors would produce tritium in lithium ceramics by the nuclear reactions such as $^6Li(n,\alpha)T$. It is known that irradiation defects are induced in the tritium breeding materials by the interaction of energetic neutrons, tritium ions and helium ions, and other processes. It has reported that these irradiation defects could affect tritium recovery processes from the tritium breeding materials [1–16]. Therefore, for the establishment of the tritium recovery system, it is one of critical issues to understand the chemical behavior of tritium produced in the tritium breeding materials including its chemical states and release behavior. Many researchers have investigated the production and annihilation of the irradiation defects such as F^+-center, which is an oxygen vacancy occupied by one electron, in various tritium breeding materials, and their effects on tritium release behavior from the tritium breeding materials [1–3,7–16].

In our previous studies, it has revealed that annihilation of the irradiation defects produced by

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neutron irradiation plays an important role in tritium release from lithium ceramics such as $LiAlO_2$, Li_2TiO_3 and Li_2ZrO_3 [2,3,16]. It was also suggested that the annihilation of irradiation defects in the lithium ceramics was closely correlated with the tritium release. Okuno et al. reported that the existing states of tritium produced in neutron-irradiated Li_2O correlated with the annihilation process of F^+-center [1]. Oyaidzu et al. reported also that the tritium release from neutron-irradiated Li_2TiO_3 began just before the irradiation defects were completely annihilated [2].

The present studies, therefore, have focused on correlation between the annihilation process of the irradiation defects and the tritium release process in neutron-irradiated Li_2SiO_3 and Li_4SiO_4, which are candidates of the ceramic tritium breeding materials. The electron spin resonance (ESR) method was employed to follow the annihilation process of the irradiation defects during isochronal and isothermal annealing experiments. The experimental results of neutron-irradiated Li_2SiO_3 were also compared with those of neutron-irradiated Li_4SiO_4. A comprehensive model was also discussed for understanding the correlation between the tritium release and annihilation processes of the irradiation defects produced in neutron-irradiated ceramic tritium breeding materials.

2. Experimental

The Li_2SiO_3 powder was purchased from Aldrich Ltd., and was sintered to use as the sample. The Li_4SiO_4 pebbles were provided from Forschungszentrum Karlsruhe (Fzk). Both samples were preheated at 673 K for 8 h and then held at that temperature for 4 h under a reduced pressure of He to remove moisture and hydroxides on/in the sample surface. The samples were then sealed in quartz capsules, and were irradiated with the thermal neutrons at a neutron flux of 2.75×10^{13} n cm^{-2} s^{-1} for 120 s at ambient temperature in the Pneumatic Tube No. 2 of Kyoto University Research Reactor Institute (KUR). Isochronal annealing experiments for neutron-irradiated samples were performed using conventional electric furnace to find the temperature region for the annihilation of the defects. The ESR (JEOL, JES-TE200) experiment was employed to observe the annihilation processes of the defects introduced by neutron irradiation. The annealing temperature for the samples was increased stepwise with steps of 25 K from room temperature to 623 K. After each annealing step, the samples were rapidly cooled down to 77 K, and then the ESR measurements were carried out. These procedures of the heat treatment and ESR measurement were sequentially repeated.

Isothermal annealing experiments for the neutron-irradiated samples were performed to establish the kinetics of the annihilation process of the irradiation defects. Based on the results of the isochronal annealing experiments, the annealing temperatures for the isothermal annealing experiment were selected to be 423, 473, 523 and 573 K for Li_2SiO_3 and 423, 523, 598 and 623 K for Li_4SiO_4. Each annealing experiment was continued up to 480 min until the ESR signals became undetectable or the signals exhibited no further change.

The tritium release experiments for the neutron-irradiated Li_4SiO_4 were performed by means of a tritium release apparatus, which was described in detail in Ref. [3]. The sample was heated from room temperature to 1073 K with a heating rate of 5 K min^{-1} by conventional electric furnace. A gas mixture of 1000 ppm H_2 diluted by N_2 was purged to scavenge the released tritium and it was measured with an ion chamber (I.C.). Memory effects in I.C. were depressed by using a 10 000 ppm H_2O diluted in N_2 gas.

3. Results and discussion

Fig. 1 shows ESR spectra for the Li_2SiO_3 sample before and after neutron irradiation. An asymmetric and rather complex ESR spectrum was observed in the neutron-irradiated sample. This suggested that

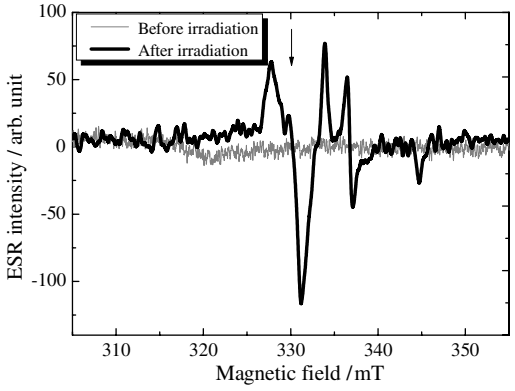

Fig. 1. ESR spectra of the Li_2SiO_3 sample before and after neutron irradiation.

various defects were produced in the sample by neutron irradiation, based on the peak analysis. It was also found from the *g*-value and the shape of the signal near 330 mT as shown by the arrow in Fig. 1 that the defect produced in neutron-irradiated Li_2SiO_3 could be identified as an E′-center, which is a congeneric defect to the F^+-center produced in neutron-irradiated Li_2O. It was presumed from the other signals that non-bridging oxygen hole center (NBOHC) as $\equiv Si–O^0$ and peroxy-radical (POR) as $\equiv Si–O–O^0$, were produced for the neutron-irradiated SiO_2 sample [4].

Fig. 2 shows the change of the ESR peak areas for Li_2SiO_3 and Li_4SiO_4, which were estimated by the double numerical integration of the ESR peak intensities at various temperatures. The figure showed that the ESR peak intensities for both samples began to decrease for isochronal annealing at 448 K and finally disappeared around 573 K. This suggested that the irradiation defects for both samples were annihilated at almost the same temperature regions, and the appropriate temperature region for the isothermal annealing experiments was between 400 K and 600 K. Therefore, isothermal annealing experiments for neutron-irradiated Li_2SiO_3 and Li_4SiO_4 were performed in this temperature range. Comparison of the annihilation curve of the irradiation defects with the tritium release curve of neutron-irradiated Li_2SiO_3 and Li_4SiO_4 are shown in Figs. 3 and 4, respectively. With regard to the tritium release for Li_2SiO_3, the experimental results obtained by Moritani and Moriyama [5] are used in Fig. 3. It was shown from the figures that the annihilation process of the irradiation defects was correlated closely with the tritium release process of both samples, because tritium release began just before the irradiation defects were completely annihilated.

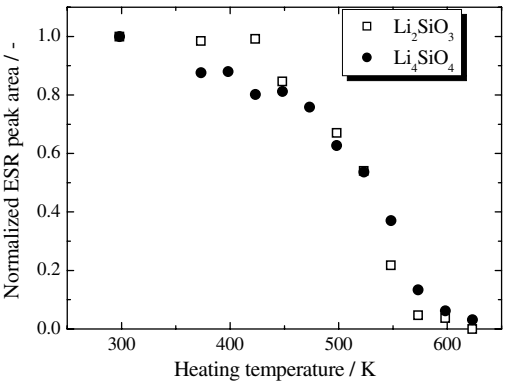

Fig. 2. Annihilation behavior of neutron irradiation defects in Li_2SiO_3 and Li_4SiO_4 for isochronal annealing experiments.

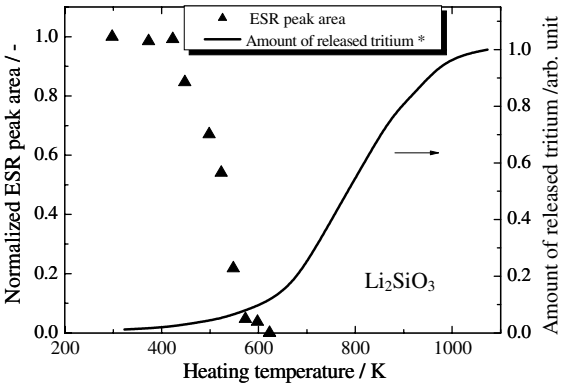

Fig. 3. Comparison of the annihilation curve of the irradiation defects with the tritium release curve of neutron-irradiated Li_2SiO_3. * Data from Moritani and Moriyama [5].

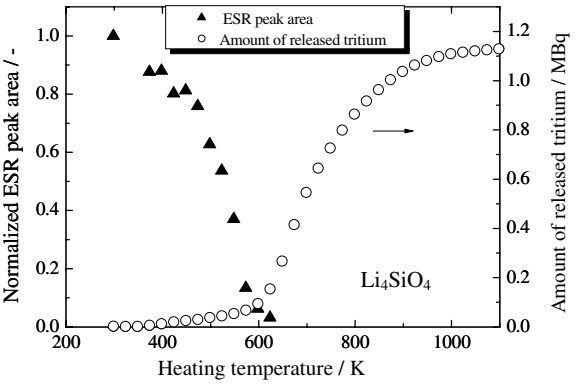

Fig. 4. Comparison of the annihilation curve of the irradiation defects with the tritium release curve of neutron-irradiated Li_4SiO_4.

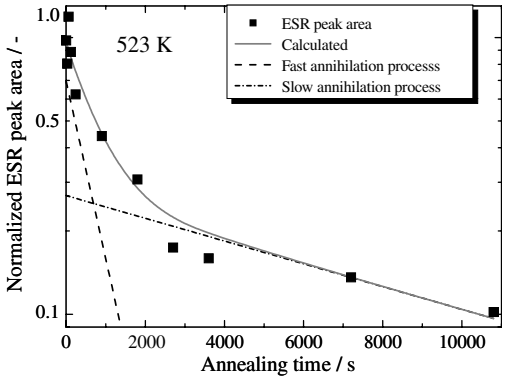

Fig. 5. Isothermal annealing curve of the ESR peak area for Li_2SiO_3 at 523 K.

Isothermal annealing curve of the ESR peak area for Li_2SiO_3 at 523 K is shown in Fig. 5. In this

figure, the annihilation processes of the irradiation defects were assumed to consist of two processes, namely a fast and slow processes. If both processes are assumed to be expression as first-order reactions, these processes are represented by the following equations:

$$[\mathrm{def}] = [a] + [b], \tag{1}$$

$$-\frac{\mathrm{d}[a]}{\mathrm{d}t} = k_\mathrm{f}[a], \tag{2}$$

$$-\frac{\mathrm{d}[b]}{\mathrm{d}t} = k_\mathrm{s}[b]. \tag{3}$$

The following Eq. (4) is derived from Eqs. (1)–(3),

$$[\mathrm{def}] = [a]^0 \exp(-k_\mathrm{f}t) + [b]^0 \exp(-k_\mathrm{s}t), \tag{4}$$

where [def] is the concentration of the defects at annealing time t, $[a]$ that of fast process, $[b]$ that of slow process, k_f the rate constant of fast process, k_s the rate constant of slow process, respectively. The values of $[a]^0$, $[b]^0$, k_f and k_s were determined by the least-squares method. Using these values, the activation energies for each process, E_f and E_s, were determined. The rate constants, k_f and k_s, represent by the following Arrhenius equation:

$$k_\mathrm{f} = A_\mathrm{f} \exp\left(-\frac{E_\mathrm{f}}{RT}\right), \tag{5}$$

$$k_\mathrm{s} = A_\mathrm{s} \exp\left(-\frac{E_\mathrm{s}}{RT}\right), \tag{6}$$

where A_f and A_s are the pre-exponential factors for each process, and R, the gas constant. The rate constants determined for Li_2SiO_3 and Li_4SiO_4 were plotted in Figs. 6 and 7, respectively. From the slope of the Arrhenius plots, the activation energies were

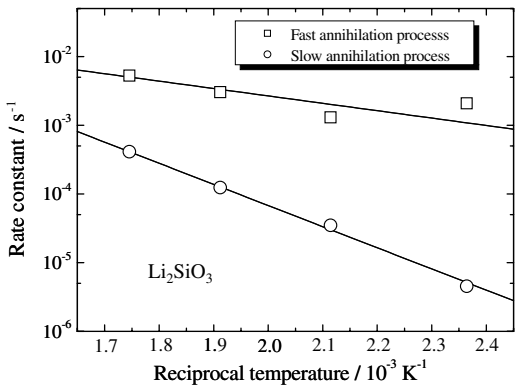

Fig. 6. Arrhenius plots for the rate constant of fast and slow annihilation processes for Li_2SiO_3.

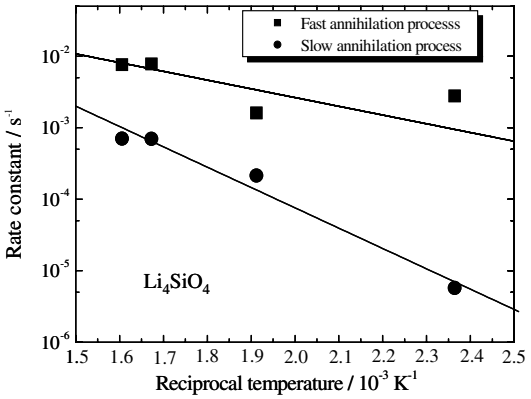

Fig. 7. Arrhenius plots for the rate constant of fast and slow annihilation processes for Li_4SiO_4.

determined to be $E_\mathrm{f} = 0.12 \pm 0.02$ eV and $E_\mathrm{s} = 0.63 \pm 0.01$ eV for Li_2SiO_3, $E_\mathrm{f} = 0.12 \pm 0.07$ eV and $E_\mathrm{s} = 0.56 \pm 0.01$ eV for Li_4SiO_4, as summarized in Table 1. It was found that the energies of the fast annihilation processes for both samples were close, whereas, those of the slow annihilation processes showed a slight difference. Based on our previous studies, the fast annihilation process may result from migration of trapped electrons to the defects. Electrons trapped in the potential valley of neutron irradiation defects could migrate and be trapped by E′-center. On the other hand, taking account of the interaction of tritium with F^+-center [1,2], the slow annihilation process could result from the annihilation of E′-center by recovering oxygen ions (O^-) to their own sites. Okuno et al. also reported that T^+ to T^- conversion would be attributed to the interaction of tritium with F^+-center and T^- to T^+ conversion would be attributed to the annihilation of F^+-center through thermal annealing in Li_2O [1]. Therefore, it can be said that the T^+ could migrate more easily to the oxygen vacancy, and trapped by the oxygen vacancy. After that, oxygen ions were thought to be recovered to their own site and E′-centers would be annihilated by forming pair electrons on oxygen (O^{2-}). The trapped tritium would be pushed out of E′-center at the same time. So,

Table 1
Activation energies of fast and slow annihilation processes for Li_2SiO_3 and Li_4SiO_4

Li_2SiO_3	Fast annihilation process	0.12 ± 0.02 eV
	Slow annihilation process	0.63 ± 0.01 eV
Li_4SiO_4	Fast annihilation process	0.12 ± 0.07 eV
	Slow annihilation process	0.56 ± 0.01 eV

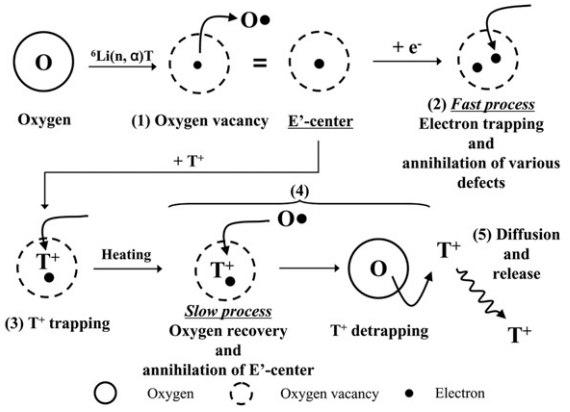

Fig. 8. A model of the annihilation of E′-center and tritium behavior.

the annihilation of E′-center by oxygen ion recovery seems to trigger the tritium release.

Based on these considerations, the following model was proposed as shown in Fig. 8. (1) Production of oxygen vacancies identified as E′-center by recoil of high energy particles generated by ^{6}Li(n,α)T. (2) Annihilation by diffusion of trapped electrons into E′-center as the fast annihilation process. (3) Tritium trapping at E′-center. At the same time, (4) Annihilation of E′-center by O^- migration ,and the tritium pushing out of the E′-center, resulting trigger the tritium detrapping as the slow annihilation process. (5) Tritium diffusion in the bulk and then tritium release by recombination or isotope exchange reaction on the sample surface.

Doremus determined the activation energy of oxygen diffusion in SiO_2 to be 1.17 eV [6]. When the oxygen ions migrated into E′-center and were relaxed by forming O^{2-}, resulting in annihilation of E′-center, an exothermic reaction would occur, and relaxation energy would be generated. The activation energy of the oxygen ion diffusion would be apparently reduced by the relaxation of the oxygen ions. Thus, we observed the activation energies of 0.63 eV for Li_2SiO_3 and 0.56 eV for Li_4SiO_4 for annihilation of E′-center. After that, the detrapped tritium diffuses with the activation energy of 0.80 eV for Li_2SiO_3 and 0.56 eV for Li_4SiO_4 as reported by Hayashi et al. [8], and then, the tritium releases from the sample.

4. Conclusions

Annihilation of irradiation defects and tritium release processes are correlated in neutron-irradiated Li_2SiO_3 and Li_4SiO_4. It was shown that the typical annihilation processes for both samples consisted of fast and slow annihilation processes, with activation energies determined to be 0.12 ± 0.02 eV and 0.63 ± 0.01 eV for Li_2SiO_3, 0.12 ± 0.07 eV and 0.56 ± 0.01 eV for Li_4SiO_4, respectively. The fast annihilation process could result from diffusion of trapped electrons into the defects mainly, whereas the slow annihilation process could be attributed to the annihilation of E′-center by recovering oxygen ions (O^-) to their own sites. When the oxygen ions migrated to E′-center and were relaxed by forming O^{2-}, an exothermic reaction occurs, and relaxation energy would be generated. The activation energy of the oxygen ion diffusion would be apparently reduced by the relaxation of the oxygen ions. The net relaxation energies were estimated to be $1.17\text{ eV} - 0.63\text{ eV} = 0.54$ eV for Li_2SiO_3 and $1.17\text{ eV} - 0.56\text{ eV} = 0.61$ eV for Li_4SiO_4.

A model of tritium behavior in neutron-irradiated ceramic tritium breeding materials is proposed. Therefore, in terms of the investigation of the kinetics of the annihilation process of irradiation defects, the annihilation of E′-center would trigger the tritium detrapping.

The slow annihilation of irradiation defects is an important process to establishment the tritium recovering and breeding system. This information would contribute for the decision of the required operating temperature limits for blanket systems for D–T fusion reactors.

References

[1] K. Okuno, H. Kudo, J. Nucl. Mater. 138 (1986) 31.
[2] M. Oyaidzu, Y. Morimoto, H. Kodama, M. Sasaki, H. Kimura, K. Munakata, M. Okada, K. Kawamoto, H. Moriyama, M. Nishikawa, K. Okuno, J. Nucl. Mater. 329–333 (2004) 1313.
[3] Y. Morimoto, S. Akahori, A. Shimada, K. Iguchi, K. Okuno, M. Nishikawa, K. Munakata, A. Baba, T. Kawagoe, H. Moriyama, K. Kawamoto, M. Okada, Fus. Technol. 39 (2001) 634.
[4] K. Moritani, Y. Teraoka, I. Takagi, H. Moriyama, J. Nucl. Mater. 329–333 (2004) 988.
[5] K. Moritani, H. Moriyama, J. Nucl. Mater. 248 (1997) 132–139.
[6] Robert H. Doremus, J. Nucl. Mater. 349 (2004) 242.
[7] K. Okuno, H. Kudo, Fus. Eng. Des. 8 (1989) 355.
[8] T. Hayashi, S. Konishi, K. Okuno, J. Nucl. Mater. 170 (1990) 60.
[9] K. Noda, K. Uchida, T. Tanifuji, S. Nasu, J. Nucl. Mater. 91 (1980) 234.
[10] H. Kudo, K. Okuno, J. Nucl. Mater. 101 (1981) 38.

[11] H. Kudo, K. Okuno, J. Nucl. Mater. 133&134 (1985) 192.
[12] K. Noda, T. Tanifuji, Y. Ishii, H. Matsui, N. Masaki, S. Nasu, H. Watanabe, J. Nucl. Mater. 141–143 (1986) 353.
[13] M. Nishikawa, T. Kinjyo, T. Ishizaka, S. Beloglazov, T. Takeishi, M. Enoeda, T. Tanifuji, J. Nucl. Mater. 335 (2004) 70.
[14] K. Moritani, T. Magari, H. Moriyama, Fus. Eng. Des. 39–40 (1998) 675.
[15] K. Munakata, Y. Yokoyama, A. Koga, N. Nakashima, S. Beloglazov, T. Takeishi, M. Nishikawa, R.D. Penzhorn, K. Kawamoto, H. Moriyama, Y. Morimoto, K. Okuno, J. Nucl. Mater. 307–311 (2002) 1451.
[16] S. Akahori, E. Tega, Y. Morimoto, K. Okuno, M. Nishikawa, K. Munakata, H. Moriyama, K. Kawamoto, M. Okada, J. Radiochem. Nucl. Chem. 255 (2003) 257.