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Correlation between annihilation of radiation defects and tritium release in Li_2TiO_3

Makoto Oyaidzu [a,*], Yasutomi Morimoto [a], Hiroshi Kodama [a], Masayoshi Sasaki [a], Hiromi Kimura [a], Kenzo Munakata [b], Moritami Okada [c], Keizo Kawamoto [c], Hirotake Moriyama [d], Masabumi Nishikawa [b], Kenji Okuno [a]

[a] *Radiochemistry Research Laboratory, Faculty of Science, Shizuoka University, 836 Ohya, Shizuoka 422-8529, Japan*
[b] *Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka 816-0811, Japan*
[c] *Research Reactor Institute, Kyoto University, 1010-1 Noda, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan*
[d] *Graduate School of Engineering, Kyoto University, Kyotodaigaku-katsura, Sakyo-ku, Kyoto, Japan*

Abstract

Thermal annihilation kinetics of radiation defects and thermal release of tritium produced in neutron-irradiated Li_2TiO_3 were studied by ESR and a thermal desorption method, respectively. Annealing experiments indicated that there were two annihilation processes of the radiation defects, the fast and the slow processes, and their activation energies were determined to be 0.43 and 0.41 eV, respectively. Taking account of the previous studies on Li_2O and Li_4SiO_4, it is suggested that the fast process is related to Li^+ diffusion, and the slow process is attributed to annihilation of oxygen vacancies. The comparison of the defects annihilation and tritium release shows that the slow process and the tritium release from bulk appear simultaneously. Hence, the annihilation of oxygen vacancy in each sample, or in any other CBMs, could play an important role in tritium release processes.

1. Introduction

There are a variety of tritium breeding materials (TBMs) that could be employed for D–T fusion reactors. They must contain lithium, because tritium is bred by the nuclear reactions $^6Li(n,\alpha)T$ and $^7Li(n,n'\alpha)T$. To design the tritium recovering system, it is very important to understand the tritium behavior in TBMs, especially the mobility in the solid and the release processes. Okuno and Kudo reported that the state of tritium in neutron-irradiated Li_2O correlated with the annihilation process of F^+-centers, which were oxygen vacancies occupied by one electron [1]. Thereafter, Akahori et al. also reported that in neutron-irradiated Li_4SiO_4, the tritium release began just before the annihilation of radiation defects was completed [2]. These studies suggest that there should be a similar correlation between annihilation of radiation defects and tritium release in any other candidate ceramic breeding materials (CBMs). However, there are few similar studies for the other candidate materials.

The present study of Li_2TiO_3, one of the most attractive candidate TBMs, investigated kinetics of the thermal annealing of radiation defects induced in neutron-irradiated Li_2TiO_3, and correlation the defects behaviors with tritium release processes.

Electron spin resonance (ESR) method was employed to follow the annihilation behavior of the radiation defects in isothermal or isochronal heating treatment. In tritium release experiments to be compared with the

* Corresponding author. Tel.: +81-54 238 6436; fax: +81-54 238 3989.
E-mail address: r0232005@ipc.shizuoka.ac.jp (M. Oyaidzu).

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annihilation processes of the radiation defects, we prepared catalytic breeder materials [3], because observation of the bulk tritium release processes is needed to compare to the behavior of radiation defects. In order to compare the present experimental results of neutron-irradiated Li_2TiO_3 with that of neutron-irradiated Li_4SiO_4 in our previous study [2], an additional experiment was also carried out for Li_4SiO_4. Ultimately, we expect to have a comprehensive model of the correlation of tritium release and annihilation of radiation defects in CBMs.

2. Experimental

Samples of Li_2TiO_3 were purchased from Nuclear Fuel Industries Ltd., and Li_4SiO_4 were provided by Research Center Karlsluhe. Palladium was deposited on the samples for tritium release experiments in the ratio of Pd/Li_2TiO_3 and Pd/Li_4SiO_4 of 0.018 and 1.6 wt%, respectively. Details of catalytic breeder are given in Ref. [3]. The samples were preheated from room temperature (RT) to 673 K for 8 h and then kept at that temperature for 4 h in a reduced pressure of He atmosphere in order to remove moisture and hydroxides on the surface. They were then sealed in quartz capsules in the same atmosphere.

Thermal neutron irradiations were carried. The samples were irradiated with thermal neutrons to a fluence of approximately 3×10^{15} cm^{-2} at ambient temperature out in the Kyoto University Research Reactor (KUR).

Isochronal annealing experiments for neutron-irradiated Li_2TiO_3 were performed to identify the temperature region where the annealing behavior could be observed clearly. ESR equipment (JEOL, JES-TE200) was used to observe the annihilation processes of radiation defects. The annealing temperature was increased stepwise from RT up to the temperature where the ESR signals became too small to be detected. After each annealing step, the sample was immediately cooled to liquid nitrogen temperature, and the ESR measurements were carried out at that temperature. Also, since the results of isochronal annealing experiments were convenient to compare to tritium release experiments, similar experiments with Li_4SiO_4 were performed to compare with the Li_2TiO_3. The goal was to find out whether they showed a similar correlation of the annihilation of defects and tritium release.

Isothermal annealing experiments for neutron-irradiated Li_2TiO_3 were performed to establish the kinetics of the annihilation of the radiation defects. The isochronal annealing temperatures were selected as 423, 473, 523, 573 and 673 K, and each annealing experiment was carried out until the ESR signals were either too small to detect or showed little further change. The measurements were carried out in the same manner as the isochronal annealing experiment.

For the same reason as for the isochronal experiment, tritium release experiments for neutron-irradiated Pd/Li_2TiO_3 and Pd/Li_4SiO_4 were performed in the tritium release apparatus, which is described in detail in Ref. [4]. The catalytic breeder samples were heated from RT to 1073 K with a heating rate of 5 K/min. The released tritium was swept by 1000 ppm H_2 in N_2, and measured with ion chambers (IC).

3. Results and discussions

Fig. 1 shows the ESR spectra of the Li_2TiO_3 samples before and after neutron irradiation. The asymmetric ESR spectrum observed in the neutron-irradiated sample suggests that there are some kinds of defects present. As this spectrum is compared with that of γ ray irradiated Li_2TiO_3 studied by Grišmanovs et al. [5], it suggests that they are different from the viewpoints of the *g*-value and the intensity of each signal. Only one *g*-value of the signals in each spectrum agrees, but the abundance disagrees, and any other *g*-values disagree in the two experiments. Thus, the signal which are found in both experiments is derived from the defect, E′-center. Hence the signals were mainly attributed to the radiation defects induced by high energetic particles generated by the nuclear reaction. Thus, E′-center in the present study is probably one electron trapped in an oxygen vacancy.

The result of isochronal annealing experiment performed with 5 min hold time was differentiated as shown in Fig. 2. However, the information under approximately 400 K would little make sense because the polyethylene tube which covers the quartz ample in which sample was encapsulated in neutron irradiation, was distorted by the heat where would beyond the

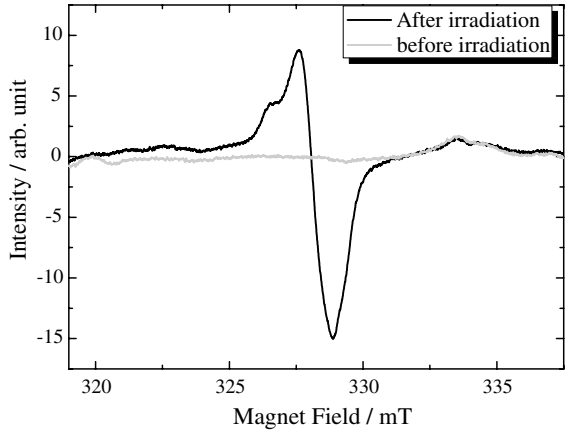

Fig. 1. ESR spectra of Li_2TiO_3 before and after neutron irradiation.

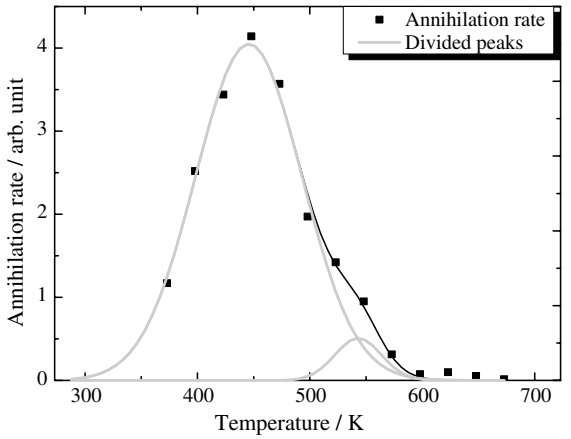

Fig. 2. The annihilation rate in isochronal annealing at intervals of 25 K for 5 min.

softening point. Thus, the appropriate temperature region for isothermal annealing experiment would be approximately from 400 to 700 K, and results can be analyzed by a Gaussian distribution function to interpret the annihilation processes. It can be seen that it consisted of two peaks; the first peak is the larger one at lower temperature region, and the second one is the smaller at higher temperature region, named Peak 1 and Peak 2, respectively. Thus, the isothermal annealing experiments were performed to interpret the kinetics of the annihilation processes of the radiation defects.

One result of the isothermal annealing experiments is shown in Fig. 3. It was also suggested that there were two annihilation processes of the radiation defects; the fast and the slow ones coincident with the isochronal annealing experimental results. The *g*-factor of peak top of ESR absorption type spectra is shifted very quickly to lower *g*-factor, and then little shift for more annealing (Fig. 4). There is a high possibility that the difference of

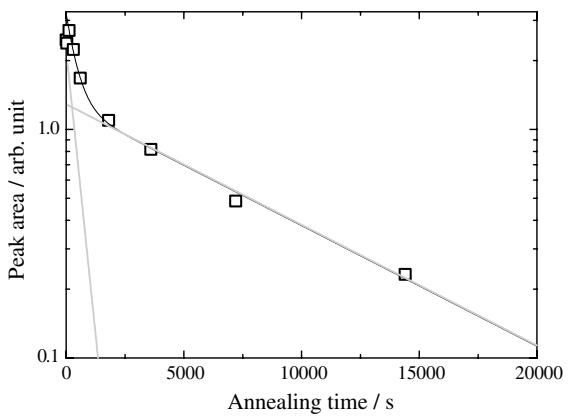

Fig. 3. Isothermal annealing at 423 K.

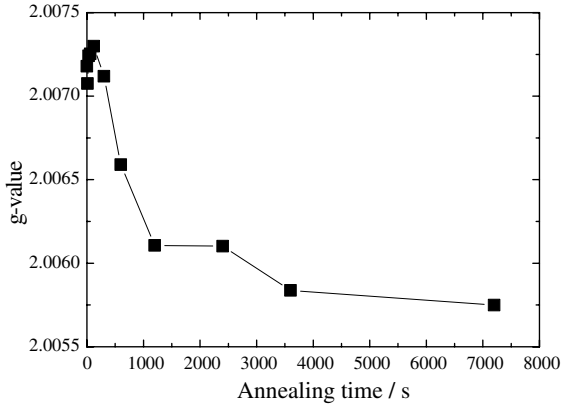

Fig. 4. Peak shift in isothermal annealing at 473 K.

the annihilation rate of defects is attributed to the difference in the radiation defects. Thus, these annealing processes could consist of two first-order reactions because detrapping or diffusion of constituent atoms or defects would be the rate-determining step in the bulk. Using the values of estimated rate constants of the fast and the slow processes for each annealing temperature, the activation energies of them are obtained by Arrhenius plot (Fig. 5), and determined to be 0.43 ± 0.01 and 0.41 ± 0.02 eV, respectively.

The results of the tritium release experiment of neutron-irradiated samples, Li_2TiO_3 and Li_4SiO_4, are shown in Figs. 6 and 7, in which the tritium release spectra were analyzed by the Gaussian distribution function, and the differentiated spectra of isochronal annealing experiments in each sample are superposed to see the correlation between the annihilation of radiation defects and the tritium release. It is found that there are two peaks between RT and 700 K in the Li_2TiO_3, three

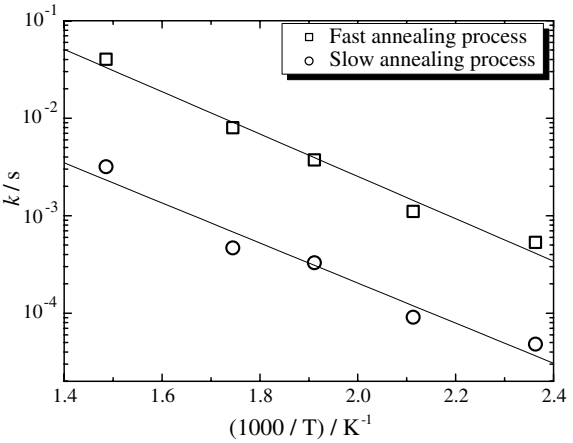

Fig. 5. Arrhenius plots for the rate constant of the fast and slow annealing processes.

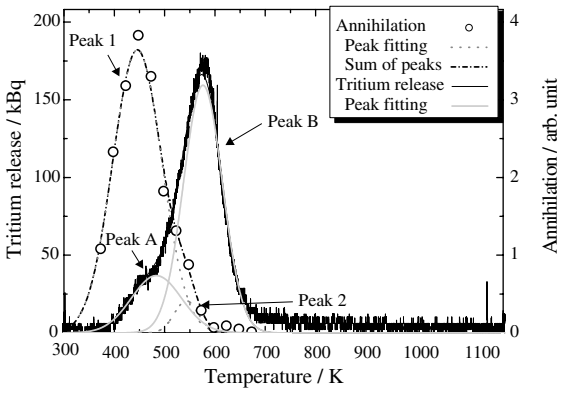

Fig. 6. Comparison of annihilation of radiation defects with tritium release in Li_2TiO_3.

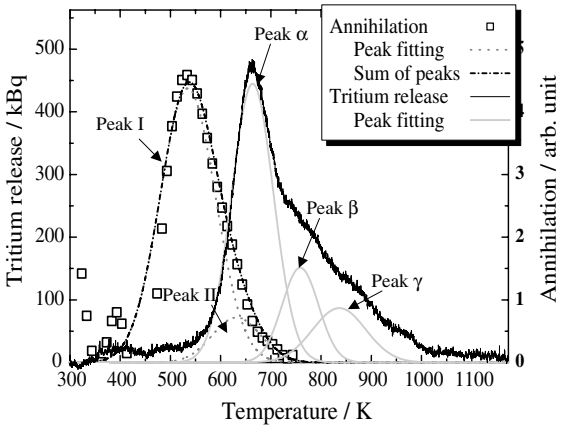

Fig. 7. Comparison of annihilation of radiation defects with tritium release in Li_4SiO_4.

peaks between RT and 1000 K in the Li_4SiO_4. The initiating temperature of the first peak of tritium release in the former, named Peak A, was lower than 400 K (near 100 °C). This result would be attributed to the irradiation annealing effect, which took place by elevation of the sample temperature during the neutron irradiation, and then the tritium would diffuse near the surface. The reason why it can little be observed in the Li_4SiO_4 is attributed to the difference of the temperature of tritium release from that considered to be bulk that the second peak of the Li_2TiO_3 (Peak B) is approximately 100 K lower than the first peak of Li_4SiO_4 (Peak α). Thus, there is one tritium release process from the bulk in the Li_2TiO_3, but three in the Li_4SiO_4. Peak B and Peak 2, or Peak α and Peak II appear simultaneously. They suggest that the oxygen vacancies annihilate in the slow process and work as tritium trapping sites, because in the Li_2TiO_3, the remaining ESR signal is attributed to the defect, E′-center, one of the oxygen vacancies and in the Li_4SiO_4, the slow process is attributed to oxygen diffusion, reported in Ref. [6], or in Li_2O, the annihilation of F^+-center, one kind of oxygen vacancy, correlate with the tritium behavior in bulk, reported in Ref. [1]. Taking account of the studies of Akahori [6] and the extremely high diffusivity of lithium ions reported in Ref. [7], the annihilation of radiation defects at Peak 1 (Fig. 6) and Peak I (Fig. 7) must be associated with lithium ion diffusion. After that, the annihilation of the remaining defects, oxygen vacancies, initiate (Peak 2 and Peak II). In the Li_4SiO_4, it is attributed to oxygen diffusion [6]; otherwise in the Li_2TiO_3, it is attributed to the diffusion of point defects with activation energy, 0.41 eV that is comparable to the activation energy of the point defect diffusivity of TiO_2, 0.40 eV, reported in Ref. [8]. The reason why the species resulting in the annihilation of defects are different in the two materials is Ti^{n+} could diffuse as point defect [8], but Si^{n+} could not. The slow process indicates the ordering of structure, and it causes the tritium release, since it annihilates oxygen vacancies working as tritium trapping sites. In short, the annihilation of oxygen vacancies is associated with the tritium release. Though the tritium release is completed in that reaction in the Li_2TiO_3, two peaks, Peak β and Peak γ, remained in the Li_4SiO_4. The difference is attributed to the thermal stability of the hydroxides, Ti–OH and Si–OH, or peroxi-hydroxide, Ti–O–OH, Si–O–OH. It is known that $Ti(OH)_4$ decompose completely by 700 K, and the peroxi-hydroxide would be less stable; otherwise, all at the latter remain in higher temperatures [2].

4. Conclusions

The tritium release processes and the annihilation of radiation defects are correlated in both neutron-irradiated Li_2TiO_3 and Li_4SiO_4. The annihilation processes of radiation defects consisted of two processes, the fast and the slow processes. The activation energies were determined to be 0.43 ± 0.01 and 0.41 ± 0.02 eV, respectively. The fast process is associated with lithium diffusion, and the slow one with diffusion of point defects in Li_2TiO_3 and oxygen diffusion in Li_4SiO_4, which recovered and annihilated the defects working as the tritium-trapping site. In the present and previous works, the annihilation process of oxygen vacancies are very important because tritium release from the bulk begin just after the slow annealing process was dominant. Therefore, the slow annihilation process of radiation defects is an important key to establishing the tritium recovering system. Similar studies of other CBMs are necessary to comprehensively define the tritium release processes. Assuming that there are similar correlation in almost all of CBMs, this information could be a reference mark to fix the temperature in blanket region in fusion reactor.

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