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Helium release from neutron-irradiated Li_2O single crystals

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Abstract

Lithium oxide (Li_2O) single crystals with various sizes (0.15–5 mm) were used as specimens. After the irradiation in JRR-4 and JRR-2 (thermal neutron fluence: 2×10^{17}–2×10^{19} n/cm^2), and fast neutrons in FFTF (fast neutron fluence: 4×10^{22} n/cm^2), helium release from the Li_2O specimens during the heating at a constant heating rate was continuously measured with a quadrupole mass spectrometer. The helium release curves from JRR-4 and JRR-2 specimens have only one broad peak each. From the dependence of the peak temperature on the neutron fluence and the crystal diameter, and the comparison with the results of sintered pellets, it is concluded that the helium generated in the crystal is released through the processes of bulk diffusion with trapping by irradiation defects such as some defect clusters. For the helium release from FFTF specimens, two broad peaks were observed in the release curves. It is considered that two different migration paths exist for helium migration in the specimen, that is, bulk diffusion and diffusion through the micro-cracks formed due to the heavy irradiation.

1. Introduction

Lithium oxide (Li_2O) is one of the prime candidates for tritium breeding material for fusion reactors. In the fusion reactor blanket environment, irradiation damage is introduced in Li_2O by energetic helium and tritium ions generated with $^6Li(n,\alpha)^3H$ reactions as well as high energy neutrons themselves. In the irradiation damage processes, it is known that helium generated forms helium bubbles in Li_2O. In the post-irradiation tests in BEATRIX-II [1] and irradiation experiments using EBR-II [2], it was suggested that the link-up of the helium bubbles forms the open pores in Li_2O and causes the large swelling. In addition, the tritium generated is considered to be trapped in the helium bubbles. Therefore, behavior of helium in Li_2O is a very important R&D issue from the standpoints of the tritium release performance and the irradiation durability which are critical for tritium breeding materials. In previous studies, the helium bubble formation in the bulk [1–3] and helium retention in the Li_2O [4,5] were investigated; however, the helium release behavior, which can provide information on helium migration behavior in Li_2O, has not been investigated. Recently, in the previous study [6], helium release measurements from Li_2O sintered pellets were carried out, and it provided some knowledge on influence of porosity and neutron irradiation on helium release behavior from sintered Li_2O with various bulk densities. In the present paper, the helium release behavior from Li_2O single crystals is investigated, and the results are discussed in the comparison with those for sintered pellets.

2. Experimental

The specimens used were Li_2O single crystals (^{6}Li enrichment; 0.07 and 7.4 at.%) of approximately 0.15–5 mm outer diameter (OD). The preparation method and properties of the single crystals are described elsewhere in detail [7,8].

Two kinds of specimens were used. One was the Li_2O single crystals (^{6}Li: 7.4 at.%) which were irradiated to 2×10^{17}, 2×10^{18} and 2×10^{19} n/cm^2 with thermal neutrons in JRR-4 and JRR-2, and the irradiation temperature was in the range of 323–373 K. The other was the Li_2O single crystals (^{6}Li: 0.07 at.%) which were irradiated in FFTF in the BEATRIX-II Phase I irradiation test. The thermal and fast (>0.1 MeV) neutron fluence were 1×10^{16} and 4×10^{22} n/cm^2, respectively,

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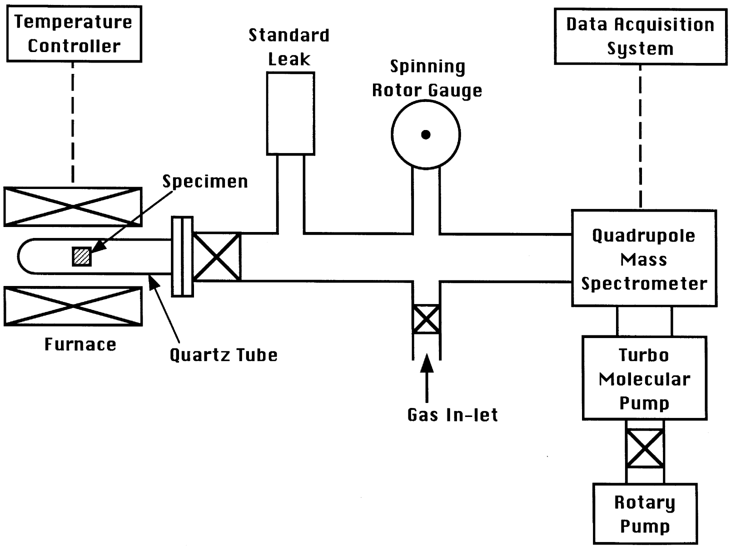

Fig. 1. Schematic diagram of helium extraction and measuring system.

and the irradiation temperature was estimated to be about 650 K.

To avoid the tritium contamination of the helium measuring system, the generated tritium in the irradiated specimens was entirely removed by the following process. The irradiated specimens were heated up to 823 K (crystal diameter below 590 μm) or 873 K (crystal diameter over 590 μm) in ammonia sweep gas at a constant heating rate of 2 or 5 K/min, and further heated at 823 K (crystal diameter below 590 μm) or 873 K (crystal diameter over 590 μm) for 2 h to confirm no retention of tritium in the specimens.

The measuring system for helium release is illustrated schematically in Fig. 1. After removing the tritium, the specimens were loaded in a quartz tube of 20 mm in diameter and heated from 823 K (crystal diameter below 590 μm) or 873 K (crystal diameter over 590 μm) to 1600 K at a constant heating rate of 2 K/min in vacuum (10^{-5}–10^{-6} Pa). During the heating, released helium was continuously measured with the pulse-counting method using a quadrupole mass spectrometer. Calibration of helium release rate was carried out using a helium standard leak and a spinning rotor gauge.

3. Results and discussion

3.1. Helium release from Li_2O single crystal irradiated with thermal neutrons

Fig. 2 shows the typical helium release curves from thermal neutron-irradiated Li_2O specimens in the constant heating rate tests. For all specimens irradiated with thermal neutrons, the helium release curves show only one broad peak in the range of 1100–1300 K. It suggests that the helium release process from Li_2O single crystals irradiated with thermal neutrons consists of only one process.

It has been clarified that the tritium release process from Li_2O single crystals irradiated with thermal neutrons consists of the bulk diffusion and surface desorption process in the previous study [9]. The helium release processes are thought to consist of the bulk diffusion and surface processes by analogy from the tritium release processes. However, the surface process can be neglected, since helium atom is inert for Li_2O and sweep gas components. Thus, only the bulk diffusion process was into account.

Fig. 3 shows the crystal diameter dependence of the temperature of the helium release peak. The crystal diameter in Fig. 3 is the average diameter of each specimen. It depicts that the temperature of the peak increases with the crystal diameter. It is considered to show that the diffusion path of the helium released is longer in the larger diameter specimens, and the bulk diffusion process is the rate determining step of the helium release process from Li_2O single crystals irradiated with thermal neutrons.

In the previous study, the helium release behavior from Li_2O sintered pellets was investigated [6]. In the helium release curves from the Li_2O sintered pellets, four kinds of peaks were observed as shown in Fig. 4. From the dependencies of the temperature of the peak on the grain diameter, bulk density and the thermal neutron fluence, and the activation energies of the peaks, it is considered that the helium migration process for peak A in Fig. 4 is the diffusion process along the grain boundary, that for peak B is the bulk diffusion process, and

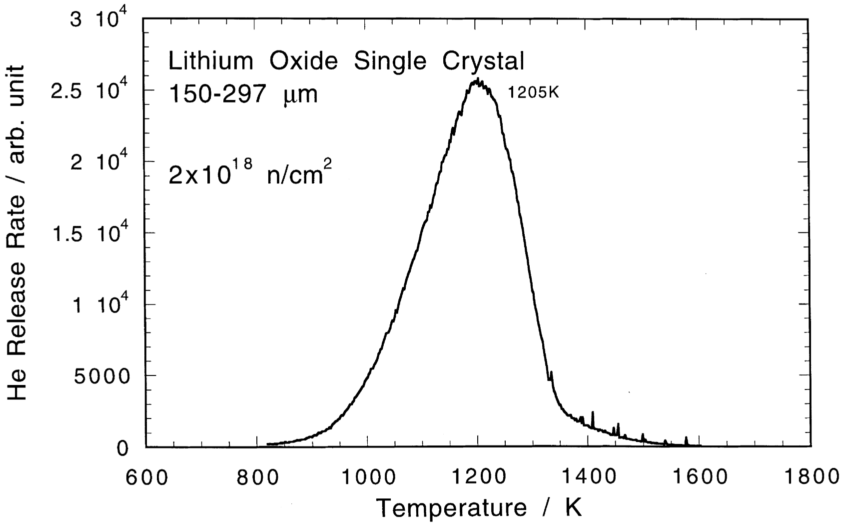

Fig. 2. Typical helium release curves from Li_2O single crystals irradiated with thermal neutrons.

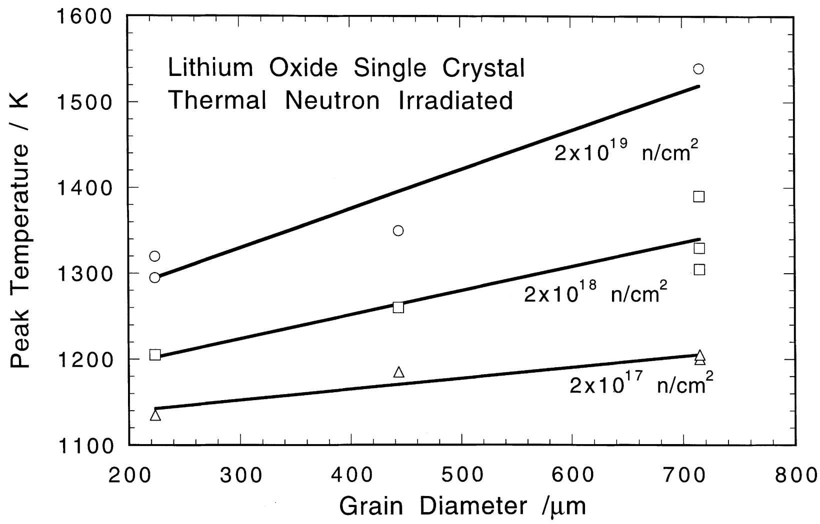

Fig. 3. The grain diameter dependence of the temperature of the helium release peaks from Li_2O single crystals irradiated with thermal neutrons.

those for peak C and D are the diffusion process with trapping at closed pores in the grains, although it has not been clarified why the two peaks C and D appear for the trapping process.

Fig. 5 shows the grain diameter dependence of the temperature of the peak B in Fig. 4 which is considered to be the peak of the bulk diffusion process, and the crystal diameter dependence of the temperature of the peak from single crystals irradiated with thermal neutrons. It is clearly shown that the temperature of both the peaks shows similar dependence on the grain and crystal diameters. It is suggested that the migration process for peak B in the helium release curves of Li_2O sintered pellets and for the peak in that of Li_2O single crystals are the same process, that is, the diffusion process in the bulk.

Fig. 6 shows the relationship between the thermal neutron fluence and the temperature of the peak in the helium release curves from Li_2O single crystals irradiated with thermal neutrons. It indicates that the temperature of the peak increases with the thermal neutron fluence. For example, the temperature of the peak for 150–297 μm specimen irradiated to 2×10^{17} n/cm^2 of thermal neutrons was 1134 K, and that for same

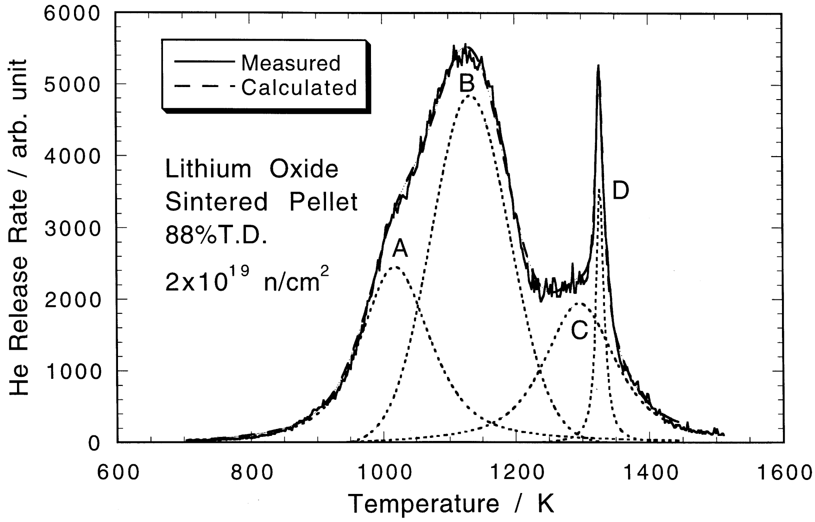

Fig. 4. The typical helium release curves from sintered Li_2O irradiated with thermal neutrons [6].

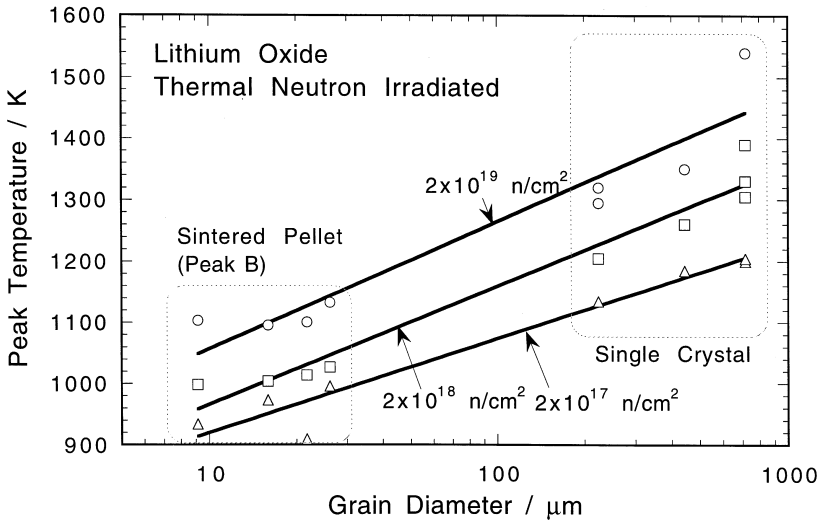

Fig. 5. The grain diameter dependence of the temperature of the peak B in Fig. 4 and that of the peak in the helium release from Li_2O single crystals irradiated with thermal neutrons.

diameter specimens irradiated to 2×10^{19} n/cm^2 of thermal neutrons was 1304 K. From the relationship between the temperature of the peak and the grain or crystal diameter shown in Fig. 5, the peak temparature of 1304 K for 150–297 μm specimen irradiated to 2×10^{19} n/cm^2 of thermal neutron is calculated to be equal to the 3080 μm crystal diameter specimen irradiated to 2×10^{17} n/cm^2 of thermal neutrons. It means that the apparent helium diffusion path for the 150–297 μm specimen irradiated to 2×10^{19} n/cm^2 thermal neutrons is about 14 times that of the specimen irradiated with 2×10^{17} n/cm^2 thermal neutrons. It seems to indicate that the helium diffusing in the Li_2O crystal is trapped at defects introduced in the crystals by the energetic helium and tritium generated by the reaction of ^{6}Li(n,α)^{3}H. Radiation damage studies performed so far showed that F^+ centers (an oxygen vacancy trapping an electron), F-aggregate centers, Li colloidal centers, etc. were introduced by irradiation. Although such irradiation defects are annealed out at the temperatures lower than 900 K [10], the irradiation effects on the peaks are still observed above 900 K, as shown in Fig. 6. Thus, the irradiation defects as trapping sites are considered not to be the above-mentioned irradiation defects such as F^+

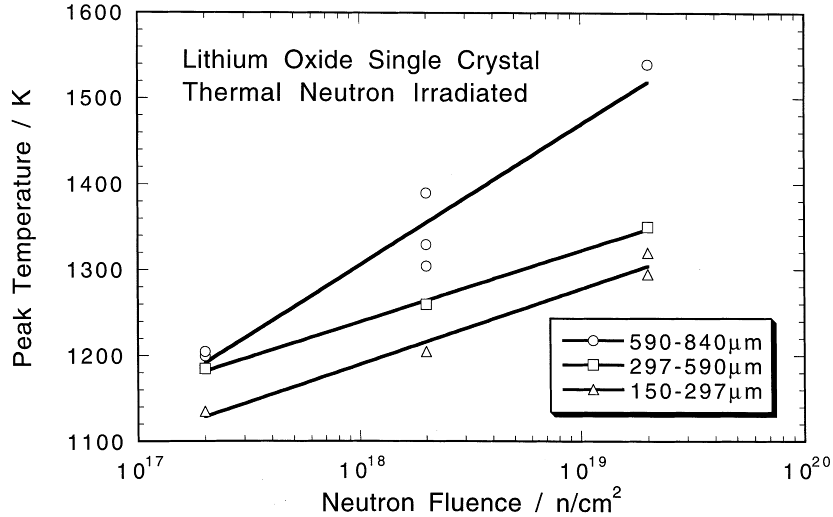

Fig. 6. The relationship between the thermal neutron fluence and the temperature of the peaks in the helium release curves from Li_2O single crystals irradiated with thermal neutrons.

centers and Li colloidal centers but some defect clusters such as dislocation loops etc. which are not completely annealed out even at 1400 K.

3.2. Helium release from Li_2O single crystal irradiated with fast neutrons

Fig. 7 shows the typical helium release curve of Li_2O single crystals (^6Li enrichment 0.07 at.%) irradiated with fast neutrons in FFTF in the constant heating rate tests. Although the helium release curves of thermal neutron irradiated Li_2O single crystals have only one peak as shown in Fig. 2, that from the Li_2O single crystals irradiated in FFTF seems to consist of two broad peaks which are superimposed by many sharp peaks as shown in Fig. 7. It is considered to show that the helium release process from Li_2O single crystals irradiated in FFTF consists of some different processes. From the comparison with the results of the helium release curves from Li_2O single crystal irradiated with thermal neutrons, it is considered that the larger broad peak in Fig. 7 (peak F) is for the bulk diffusion process.

Since helium atom is inert for Li_2O and sweep gas components as mentioned previously, the existence of

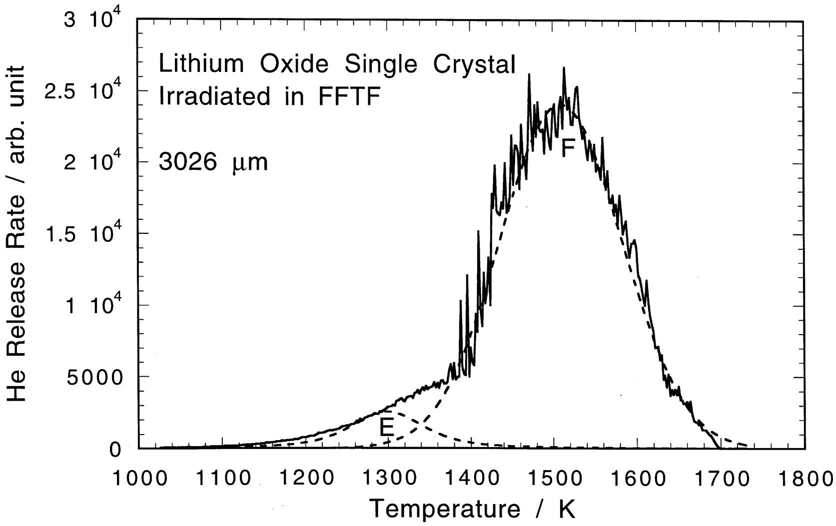

Fig. 7. The typical helium release curve from Li_2O single crystals irradiated with fast neutrons in FFTF.

the two broad peaks in the helium release curve suggests that the two different diffusion processes exist in the helium release. Although further investigations of micro-structure of the specimen using SEM, etc. are necessary, there is a possibility that the diffusion through the micro cracks formed due to heavy irradiation in FFTF with fast neutrons may be the process for the peak E.

In the helium release curves, many sharp peaks are superimposed on the broad two peaks as shown in Fig. 7. In the PIE of BEATRIX-II Phase I, no helium bubble formation was observed in the specimens [11]. Baldwin et al. indicated that the retained helium in Li_2O sintered pellets irradiated with fast neutrons in EBR-II are 12–25% of the generated helium at the irradiation temperature of 773 and 973 K, while 5–10% at 1173 K [5]. In the PIE of BEATRIX-II Phase II irradiation tests, it was found that helium bubbles were grown-up in the irradiation temperature range of 803–913 K for Li_2O sintered ring specimens [1]. In addition, extensive bubble formation was observed after heating in an inert atmosphere to 1223 K for 1 h by Verrall et al. [3]. Therefore, it is considered that the temperature of the FFTF specimen examined in the PIE of BEATRIX-II Phase I is not high enough to form helium bubbles in the grain since the temperature of the specimen during and after irradiation was kept below 650 K [11]. Since the specimens used in this study had been heated up to over 800 K before this study to remove the generated tritium in the specimen, it is considered that the helium bubble could be formed during the tritium removal process. Thus it is considered that the superimposed sharp peaks may have appeared due to the burst of the trapped helium in the bubbles through the cracking of crystal which was induced by heating up to high temperatures during the measurement of helium release.

4. Conclusion

Helium release behavior in post-irradiation heating tests was investigated for Li_2O single crystals which had been irradiated with thermal neutrons in JRR-4 and JRR-2, and fast neutrons in FFTF. It is clarified that the helium release curves from JRR-4 and JRR-2 specimens consist of only one broad peak. From the dependence of the peak temperature on the neutron fluence and the crystal diameter, and the comparison with the results obtained for sintered pellets, it is considered that the helium generated in the specimen is released through the process of bulk diffusion with trapping by irradiation defects such as some defect clusters. For the helium release from FFTF specimens, two broad peaks were observed in the release curves. It is suggested that two different diffusion paths exist for helium migration in the specimen, that is, bulk diffusion and diffusion through the micro-crack due to the heavy irradiation. In addition, helium bubble formation after irradiation caused by the heating up to high temperature over 800 K is suggested.

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