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Tritium release behavior from neutron-irradiated Li_2TiO_3 single crystal

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Abstract

Li_2TiO_3 single crystals with various grain size (1–2 mm) were used as specimens. After the irradiation up to 4×10^{18} n/cm^2 with thermal neutrons in JRR-2, tritium release from the Li_2TiO_3 specimens in isothermal heating tests was continuously measured with a proportional counter. The tritium release in the range from 625 to 1373 K seems to be controlled by bulk diffusion. The tritium effective diffusion coefficient (D_T) in Li_2TiO_3 was evaluated to be $D_T[\mathrm{cm}^2/\mathrm{s}] = 0.100 \exp(-104[\mathrm{kJ/mol}]/RT)$, 625 K $< T <$ 1373 K. In this temperature region, the tritium effective diffusion coefficients in Li_2TiO_3 are close to those of Li_2O irradiated with thermal neutrons of 4×10^{16} and 2×10^{19} n/cm^2. It indicates that the tritium release performance of Li_2TiO_3 is essentially as good as that of Li_2O.

1. Introduction

Li_2TiO_3 is a promising candidate for tritium breeding material because of its low activation, excellent tritium release performance, chemical stability, etc. [1,2]. In a previous study [3], Li_2TiO_3 sintered pellets were prepared and characterized. This study showed that compatibility of Li_2TiO_3 with stainless steel (HT-9, 316SS) is better than that of Li_2O and Li_2ZrO_3, and that tritium release performance of Li_2TiO_3 is better than that of Li_2ZrO_3 and similar to that of Li_2O.The tritium release processes in ceramic breeders consist of bulk diffusion, grain boundary diffusion, surface desorption, etc. Recently, tritium release behavior from sintered Li_2TiO_3 was investigated [1,2,4–8]. It has been reported that the tritium release behavior from sintered Li_2TiO_3 is influenced by the bulk density, grain size, surface condition, sweep gas composition, etc., and that the rate determining process of tritium release from Li_2TiO_3 sintered pellets is the surface desorption of adsorbed tritium [4,5]. However, irradiation effects on the diffusion and surface desorption processes should be taken into account to evaluate the tritium release performance of the materials in a fusion blanket environment, where ceramic breeders are subjected to severe neutron irradiation. From this standpoint, tritium diffusivity in bulk is required as one of the baseline properties data. For the investigation on diffusion process, single crystal specimens are recommended to be used since contributions from surface desorption/adsorption are minimized. Previously, tritium diffusivity in Li_2O was evaluated by measuring tritium release from single crystals, and furthermore the irradiation effects on tritium diffusion behavior were investigated at various neutron fluence levels [9,10]. In the present paper, Li_2TiO_3 single crystal was prepared, and the tritium release behavior from the Li_2TiO_3 single crystal was investigated to obtain tritium diffusivity in the bulk.

2. Experimental

The starting material is Li_2TiO_3 powder (98% pure) purchased from Cerac/Pure, inc. Fused Li_2TiO_3 rods with coarse crystal grains were obtained from the sintered rod prepared from the powder by a floating zone (FZ) apparatus using infrared imaging furnace. The fused Li_2TiO_3 rod was heated at 1173 K for 1 h in air in

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order to anneal out color centers introduced during fabrication of the fused rod. The X-ray diffraction pattern of the fused rod showed Li_2TiO_3 with monoclinic crystal structure. The microstructure observations by an optical microscope and a scanning electron microscope showed some grains of about 1–2 mm in size. The Li_2TiO_3 single crystals were obtained from the fused Li_2TiO_3 rod which was subjected to the above-mentioned annealing. The Li_2TiO_3 single crystals were crushed into small fragments (1–14 mg). The preparation and characterization of the Li_2TiO_3 single crystals used as specimens are described elsewhere in detail [11].

The Li_2TiO_3 single crystal specimens were irradiated with thermal neutrons in JRR-2 up to 4×10^{18} n/cm^2 at ambient temperature (about 350 K). After irradiation, the tritium release from the specimen was measured in a flow (180 cm^3/min) of ammonia(NH_3) sweep gas at atmospheric pressure during isothermal annealing between 625 and 1373 K with a proportional counter. The measuring system is schematically illustrated in Fig. 1.

In order to heat the specimens up to the desired temperature as quickly as possible, the isothermal annealing was carried out in the following manner. A platinum crucible containing the specimens was temporarily held in a silicon rubber tube with a clamp. After the desired temperature of the furnace was attained, the crucible was dropped into the furnace. After about 1 min, the maximum release rate was observed. Behavior of the tritium release was analyzed by assuming that the release started at the time when the maximum release rate was observed. In the measuring system, the counter was kept at about 380 K to suppress its contamination of the due to adsorption of tritium. The background signal of the counter was $1–2 \times 10^2$ cpm before and after every run.

3. Results and discussion

3.1. Effects of sweep gas composition

In order to investigate the tritium diffusion process in Li_2TiO_3, it is necessary to minimize the tritium inventory on the Li_2TiO_3 surface. It is known that the control the composition of tritium sweep gas, such as an addition of hydrogen to helium, is very effective in minimizing the surface tritium inventory of lithium ceramics. Therefore, it is important to select the optimum sweep gas composition for minimizing the surface inventory. For selection of the sweep gas used in the tritium release experiments for Li_2TiO_3 single crystals, the effects of the sweep gas composition on tritium release behavior were investigated by using sintered Li_2TiO_3 (81%T.D.) irradiated with thermal neutrons up to 1×10^{17} n/cm^2. After the irradiation, the tritium release behavior was observed in constant heating rate tests of 10 K/min by using pure H_2, He–1%H_2, pure He and pure NH_3 sweep gases. As shown in Fig. 2, three peaks appeared around 620, 700 and 870 K in the tritium release curves for all sweep gases. The tritium release from sintered Li_2TiO_3 was shown to be controlled by surface desorption process [6], and therefore three peaks are considered to be

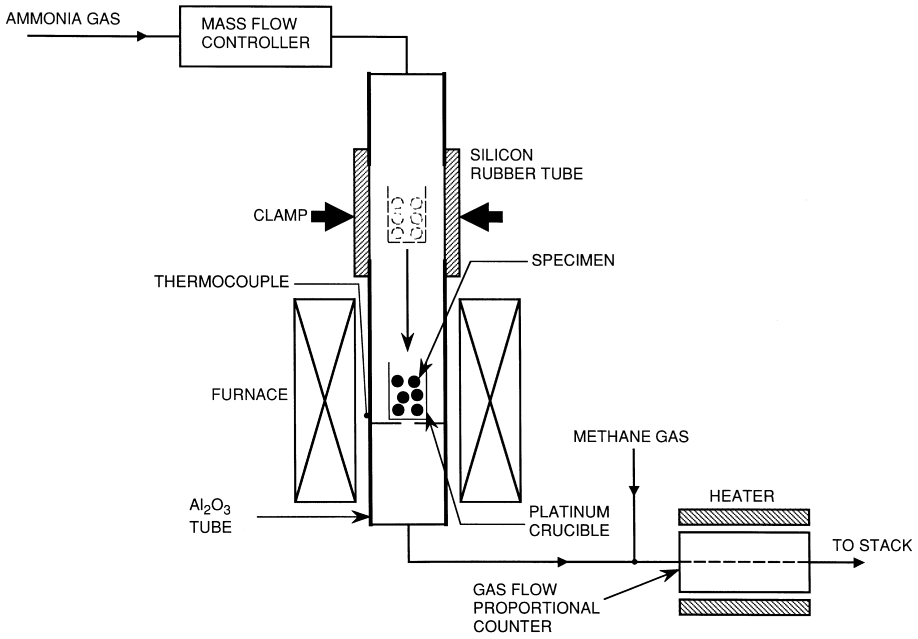

Fig. 1. Schematic diagram of tritium extraction and measuring system.

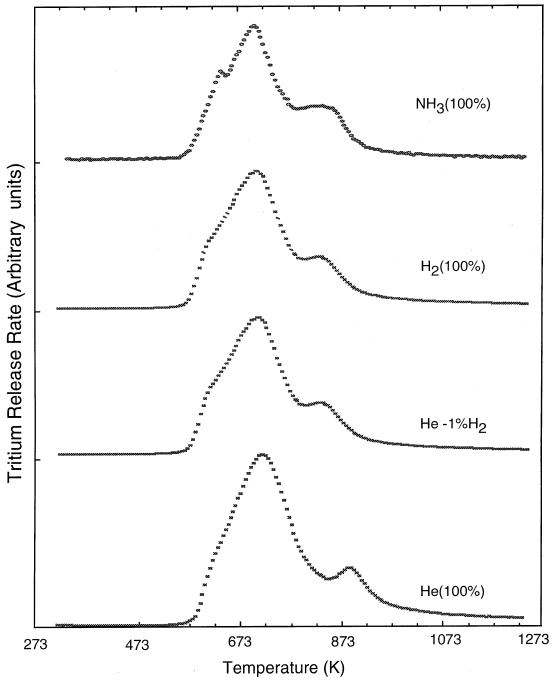

Fig. 2. Release behavior from sintered pellet during constant heating rate of 10 K/min in the case of pure NH_3, pure H_2, He–1%H_2 and pure He.

due to the surface process (see Fig. 3). In the comparison among the four sweep gases, the lowest temperature peak around 620 K is most clearly separated from other peaks for pure NH_3 sweep gas. It is indicate that the tritium release rate from the sintered Li_2TiO_3 is the largest in case of the pure NH_3 sweep gas. This means the pure NH_3 more effectively sweeps the surface tritium than the other three sweep gases. It is known that NH_3 does not react chemically with Li_2TiO_3. Therefore, the pure NH_3 sweep gas was used in the Li_2TiO_3 single crystal experiments.

3.2. Tritium release from Li_2TiO_3 single crystals

The isothermal heating tests were performed in the range from 625 to 1373 K for Li_2TiO_3 single crystals (weight: 1–14 mg) irradiated with thermal neutrons. In the calculation of diffusion coefficient of tritium, it is assumed that the specimens which had irregular shapes were spheres with various radii as a first approximation. When the tritium is controlled by the diffusion process in the specimens, the fraction of released tritium (f) can be expressed by

$$f = 1 - (6/\pi)\sum_{n=1}^{\infty}(1/n^2)\exp\left(-n^2\pi^2 D' t\right), \tag{1}$$

where t is the time of the isothermal heating, $D' = D_T/a^2$, D_T the diffusion coefficient of tritium and a the radii of the spherical specimens.

The D' value can be obtained by use of a nomograph, as was reported by Guggi et al. [12]. When $\phi(t)$ is defined to be

$$\phi(t) = \left(6/\pi^{0.5}\right)(D't)^{0.5} \tag{2}$$

and substituted in Eq. (1), the result is

$$f = 1 - (6/\pi)\sum_{n=1}^{\infty}\left(1/n^2\right)\exp\left(-n^2\pi^3\phi(t)^2/36\right). \tag{3}$$

Using Eq. (3), $\phi(t)$ can be calculated from the values of f obtained. Fig. 4 shows typical log–log plots of $\phi(t)$ versus heating time. These plots show linear relationship with slope of 0.5. This indicates that the tritium release is controlled by the diffusion process of tritium in the crystals, as described by Guggi et al. [12]. Fig. 5 and

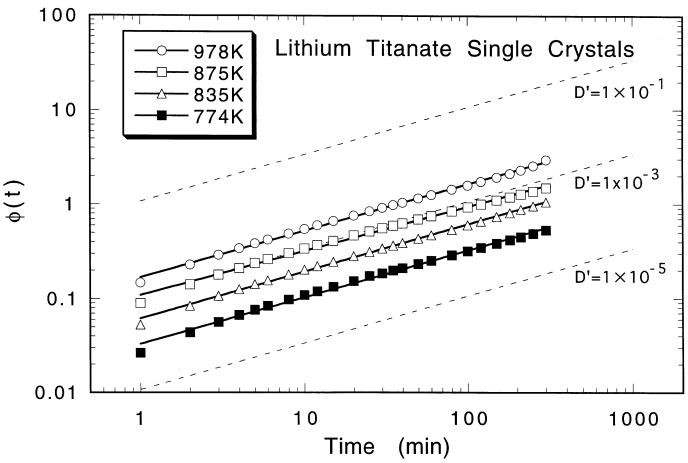

Fig. 3. Nomographic presentation of fractional release of tritium from Li_2TiO_3 single crystals irradiated with thermal neutrons.

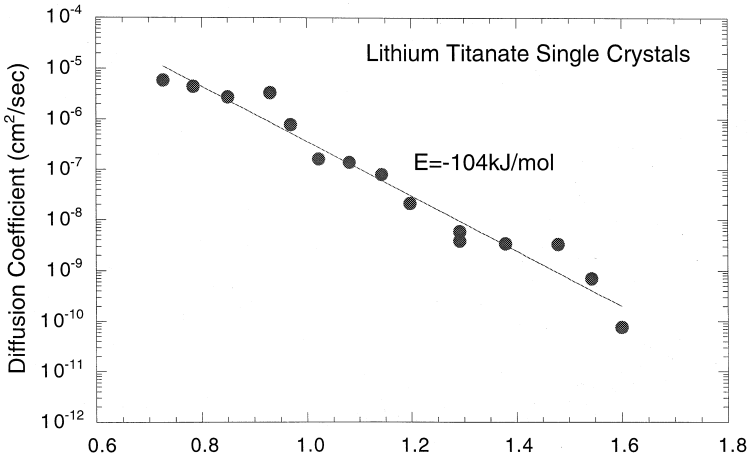

Fig. 4. The diffusion coefficients of tritium in Li_2TiO_3 single crystals.

Table 1 show the diffusion coefficients of tritium in Li_2TiO_3 single crystals, which were estimated from relationships between $\phi(t)$ and annealing time, as a function of reciprocal temperature. The estimated diffusion coefficient of tritium in Li_2TiO_3 single crystals (D_T) is described as

$$D_T\,[\mathrm{cm}^2/\mathrm{sec}] = 0.100\exp(-104[\mathrm{kJ/mol}]/RT), \quad 625\ \mathrm{K} < T < 1376\ \mathrm{K}.$$

In the previous study, the tritium release behavior was examined in the range of 650–1600 K for Li_2O single crystals with crystal size from 150 to 3050 μm which were subjected to thermal neutron irradiation at 4×10^{16} n/cm^2 and 2×10^{19} and fast neutron irradiation at 4×10^{22} n/cm^2. It was suggested by thermal neutron irradiation mentioned above (i.e. slope $\phi(t) \propto t^{-0.5}$) that the rate determining step of tritium release from Li_2O single crystals was bulk diffusion.The tritium diffusion coefficients were evaluated for Li_2O subjected to different level of irradiation. Bertone [13] evaluated the rate-determining step of the tritium release from Li_2O as a function of particle radius and temperature. Most of the experimental conditions examined for Li_2O single crystals in the above-mentioned study were found to belong to the "region of diffusional control" defined by Bertone. Thus, experimental result that tritium release in Li_2O crystals examined is controlled by bulk diffusion is supported by Bertone criterion.

In the present experiments, the crystal diameters of Li_2TiO_3 specimens were 880–1990 μm, which were calculated using the density value and the temperature range 625–1373 K. It is known that the affinity of tritiated water for Li_2TiO_3 surface is much smaller than that for Li_2O surface. Therefore, the threshold crystal

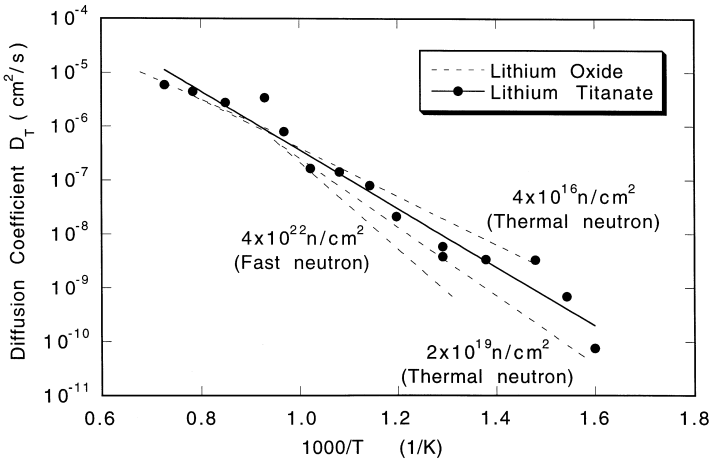

Fig. 5. Comparison of tritium diffusion coefficients in Li_2TiO_3 and Li_2O single crystals.

Table 1
Diffusion data obtained from Li_2TiO_3 single crystals

Temperature (K)	Weight (mg)	Average grain size (mm)	D' (s^{-1})	D_T (cm^2/s)
625	1.85	0.101	3.0×10^{-8}	7.7×10^{-10}
648	1.78	0.099	2.8×10^{-7}	7.0×10^{-10}
676	1.22	0.088	1.7×10^{-6}	3.3×10^{-9}
725	2.85	0.117	1.0×10^{-6}	3.4×10^{-9}
774	2.29	0.108	2.0×10^{-6}	5.9×10^{-9}
774	1.86	0.101	1.5×10^{-6}	3.8×10^{-9}
835	3.47	0.125	5.5×10^{-6}	2.1×10^{-8}
875	7.32	0.160	1.3×10^{-5}	8.3×10^{-8}
925	1.89	0.102	5.5×10^{-5}	1.4×10^{-7}
978	3.82	0.129	4.0×10^{-5}	1.7×10^{-7}
1032	4.55	0.136	1.7×10^{-4}	7.9×10^{-7}
1075	6.11	0.150	6.0×10^{-4}	3.4×10^{-6}
1176	9.62	0.175	3.6×10^{-4}	2.8×10^{-6}
1276	10.49	0.180	5.5×10^{-4}	4.5×10^{-6}
1373	14.16	0.199	6.0×10^{-4}	5.9×10^{-6}

size for the region in which the rate-determining step of tritium release processes is bulk diffusion is much smaller for Li_2O. This means that the examined experimental condition for Li_2TiO_3 belongs to the "region of diffusion control" which was defined by Bertone.

Fig. 5 shows comparison among tritium diffusion coefficient as a function reciprocal temperatures for Li_2TiO_3 and those for Li_2O irradiated with thermal and fast neutrons. The activation energies of the tritium diffusion coefficients in Li_2O single crystals subjected to thermal neutron irradiation at 4×10^{16} n/cm^2, thermal neutron irradiation at 2×10^{19} n/cm^2 and fast neutron irradiation at 4×10^{22} n/cm^2 are 82, 108 and 156 kJ/mol (<1060 K), respectively. The tritium diffusion coefficient in Li_2TiO_3 single crystals irradiated with 4×10^{18} n/cm^2 of thermal neutrons is close to those of Li_2O single crystals irradiated with thermal neutrons of 4×10^{16} and 2×10^{19} n/cm^2, that is rather larger than that of 2×10^{19} n/cm^2 and rather smaller than that of 4×10^{16} n/cm^2. The activation energy 104 kJ/mol for Li_2TiO_3 is similar to that of Li_2O single crystals irradiated with 2×10^{19} n/cm^2 of thermal neutrons equal to 108 kJ/mol.

It is suggested that the mobility of the tritium in Li_2TiO_3 is close to that in Li_2O. The affinity of H_2O with Li_2TiO_3 is much smaller than that for Li_2O. The use of Li_2TiO_3 at low temperatures (<570 K) is expected for blanket design, while the operating temperature of Li_2O in the blanket is designed to be higher than 670 K from concern for formation of LiOT. It is seen from the neutron fluence dependence on tritium diffusivity in Fig. 5 that irradiation damage has a large influence on tritium diffusion process. In general, irradiation damage does not tend to recover at low temperatures. Therefore, the data on irradiation effects on tritium diffusivity in Li_2TiO_3 is required for evaluation of tritium release performance in the fusion blanket, and will be obtained in near future.

4. Conclusion

Tritium release behavior in post-irradiation heating tests was investigated for Li_2TiO_3 single crystals which had been irradiated with thermal neutrons in JRR-2 up to 4×10^{18} n/cm^2. The tritium release in the range from 625 to 1373 K seems to be controlled by diffusion within the crystals. The tritium effective diffusion coefficient (D_T) in Li_2TiO_3 was evaluated as $D_T[cm^2/s] = 0.100 \exp(-104[kJ/mol]/RT)$, $625\ K < T < 1373\ K$. In this temperature region, the tritium effective diffusion coefficient in Li_2TiO_3 is close to those of Li_2O irradiated with thermal neutrons of 4×10^{16} and 2×10^{19} n/cm^2. It indicates that the tritium release performance of Li_2TiO_3 is essentially as good as that of Li_2O. Li_2TiO_3 is considered to be one of the promising candidate as a ceramic breeding material for fusion reactors, although neutron irradiation tests at high burnup/high dpa are needed for Li_2TiO_3.

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