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Release kinetics of tritium generated in lithium-enriched $Li_{2+x}TiO_3$ by thermal neutron irradiation

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ABSTRACT

Tritium release kinetics for $Li_{2+x}TiO_3$, the lithium-enriched Li_2TiO_3, was investigated by isochronal and isothermal annealing experiments. Tritium release by isochronal annealing showed that the dominant release stage was found at around 600 K. An additional release stage at lower temperature side was appeared with increasing excess lithium, which was attributed to the release of tritium trapped in Li_4TiO_4 structure. The dominant release stage was considered to a release of tritium trapped by irradiation defects. Isothermal annealing experiments indicated that tritium releases were controlled by diffusion process. The diffusion coefficient of $Li_{2.0}TiO_3$ was one order of magnitude as large as those of $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$, although their activation energies were almost the same. These results showed that rate-determining step was the diffusion process of tritium in Li_2TiO_3 structure for $Li_{2+x}TiO_3$ and excess lithium would make diffusion coefficient smaller. Simulation of tritium-TDS spectra for $Li_{2.0}TiO_3$ has clarified that the TDS spectrum for$Li_{2.0}TiO_3$ can be demonstrated by using Arrhenius diffusion parameters obtained by isothermal annealing experiment in the present study.

1. Introduction

For the development of D–T fusion reactors, it is important to establish an effective fuel recycling system and a comprehensive model of tritium migration processes in solid tritium breeding materials. In the test blanket module for ITER, lithium titanate (Li_2TiO_3), one of ternary lithium oxides, is a candidate as tritium breeding materials due to good tritium release property, chemical stability, and so on. In operation of D–T fusion reactor, energetic tritium is generated by the reactions of $^6Li(n, \alpha)T$ and $^7Li(n, n\alpha)T$ in Li_2TiO_3. Lithium will be consumed by these reactions, leading lithium-depletions in Li_2TiO_3 with the reactor operation. Lithium-depletion in Li_2TiO_3 induces not only lower tritium generation rate but also change of Li_2TiO_3 structures. Therefore, it is planned in future fusion reactor to replace the lithium-depleted tritium breeding materials after certain periods of operations. To improve the life cycle of tritium breeding materials with respect to tritium generation property, the use of $Li_{2+x}TiO_3$ ($x = 0.2, 0.4$), which is the lithium-enriched Li_2TiO_3, is proposed recently [1–3].

$Li_{2+x}TiO_3$ is consisted of Li_2TiO_3 structure with excess lithium. Hara et al. reported that Li_2TiO_3 and Li_4TiO_4 structures were co-existed in both of $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ although only the Li_2TiO_3 structure was found for $Li_{2.0}TiO_3$, indicating that excess lithium induced the formation of Li_4TiO_4 structure in Li_2TiO_3 during fabrication processes [4]. It is expected that tritium behavior in $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ will be different from that in Li_2TiO_3 because the structure of Li_4TiO_4 would affect on tritium behaviors. This difference on structure will be one of key issues for the use of $Li_{2+x}TiO_3$ as tritium breeding material in future fusion reactor.

Many researchers have been investigated the tritium release behaviors for several tritium breeding materials irradiated by thermal neutron [5–7]. In particular, Okuno and Kudo have been reported that tritium release kinetics for tritium breeding materials were controlled by diffusion processes [8]. The Arrhenius parameters on tritium diffusion for Li_2TiO_3 were also reported by several researchers [9,10]. However, diffusion coefficients reported by several investigators were different in a few orders, indicating that the database on tritium diffusivity in Li_2TiO_3 is not enough. Therefore, kinetic of tritium diffusivity in Li_2TiO_3 are further necessary. In this study, thermal neutron irradiation was carried out for the investigation of tritium diffusivities in $Li_{2+x}TiO_3$ ($x = 0$, 0.2, 0.4). Thereafter, out-of-pile tritium release experiments under isochronal and isothermal heating were performed. Comparing Arrhenius parameters of tritium diffusion in these materials, the effects of excess lithium on tritium release were also discussed.

2. Experimental

Powders of $Li_{2+x}TiO_3$ purchased from Kaken Co. were used as samples. The average grain diameters of $Li_{2.0}TiO_3$, $Li_{2.2}TiO_3$ and

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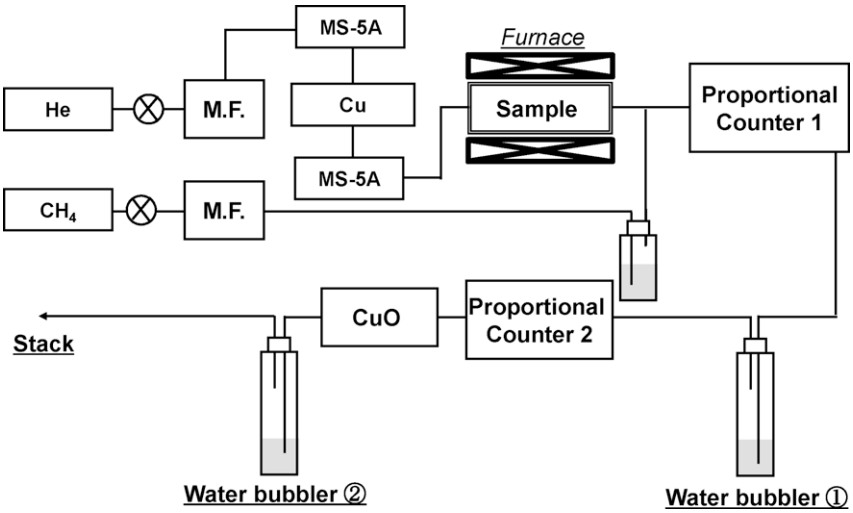

Fig. 1. Schematic drawing of tritium-TDS system.

$Li_{2.4}TiO_3$ measured by SEM were 3.0, 1.0 and 1.0 μm, respectively. 0.3 g of these samples were introduced into quartz tubes individually and annealed at 1173 K for 3 h under He gas in the pressure of less than a few Pa. After heating, these tubes were sealed. Thermal neutron irradiations were conducted at Pneumatic tube 2 (Pn-2) of Research Reactor Institute, Kyoto University (KURRI). The thermal neutron flux was 5.5×10^{12} n cm^{-2} s^{-1}. The thermal neutron irradiation was carried out for 100 min, corresponding to the thermal neutron fluence of 3.3×10^{15} n cm^{-2}. The temperature of samples during irradiation was estimated less than 350 K. Out-of-pile tritium release experiments were performed in tritium-TDS (Thermal Desorption Spectroscopy) system at Shizuoka University as shown in Fig. 1. This system has two proportional counters. The released tritium is recovered by purge gas and is carried to the first proportional counter (PC1). After PC1, purge gas with tritium passes through first water bubbler (WB1) to trap the water-form tritium such as HTO and T_2O, named as "oxidized T". The second proportional counter (PC2) set after WB1 observes gas-form tritium such as HT and T_2, named as "reduced T". Thereafter, the reduced T are oxidized by CuO with temperature of 623 K after PC2 and trapped by second water bubbler (WB2). The amounts of oxidized T and reduced T trapped in WB1 and WB2, respectively, are quantified by a Liquid Scintillation Counter.

A quartz tube with the neutron irradiated samples was set in the tritium-TDS system. Thereafter, the quartz tube was broken under purging He gas. Therefore tritium released during neutron irradiation, named as "free T" could be recovered. After recovery of free T, the sample was set into the tritium-TDS system.

In isochronal annealing experiments, the Mo crucibles with the sample were put into quartz tube set in the electric furnace. The thermo-couple was set in the furnace. The isochronal annealing was carried out from room temperature to 1173 K with a heating rate of 0.5 K/min (0.0083 K/s). The He gas with the flow rate of 15 sccm was introduced into MS-5A and a heated Cu at 623 K to exclude impurity such as water and oxygen in He gas bottle, and then purged into the system during the experiment. The CH_4 gas with the purging rate of 25 sccm was also used as a counting gas for the proportional counters. The CH_4 gas was made wet by passing through another water bubbler for reduction of memory effect in proportional counters. Wet CH_4 gas was converged to He gas flow just before PC1 so that wet CH_4 is not purged directly to Mo crucible with sample during heating. The quartz tube and pipes after furnace and the proportional counters were also heated at around 373 K to reduce memory effect.

Isothermal annealing experiments were carried out in the following manners in order to heat the samples up to the desired temperature as quickly as possible. The Mo crucible inside of quartz tube was set in furnace. At first Mo crucible in quartz tube was fixed at out of furnace where heat from furnace does not reach. After achievement of desired furnace temperature, Mo crucible was moved into heated region. Isothermal annealing was conducted around 500–600 K.

3. Results and discussion

The amounts of tritium recovered from 0.3 g of $Li_{2.0}TiO_3$, $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ were 1.4, 1.6 and 1.7 MBq, respectively. These amounts of tritium were consistent with amounts of bred tritium calculated from thermal neutron fluence. The fractions of free T, oxidized T and reduced T are listed in Table 1. Almost of all free T was the oxidized form like HTO and its fraction was less than 10% in total tritium produced in $Li_{2+x}TiO_3$. The fraction of free T was increased with increasing excess lithium concentration, namely value of x. About 70% of tritium was release as oxidized T. Many previous out-of-pile experiments showed most of tritium generated in tritium breeder was release as oxidized form [8,12,13]. Tritium release as oxidized form was caused by the reaction of tritium with oxygen such as dissolved and/or adsorbed on surface of breeder materials. Because the amount of generated tritium in breeder materials is quite small compared to that of breeder material (in present case, molecular ratio: $T/Li_2TiO_3 = 10^{-6}$), most of tritium was reacted with surface oxygen during release processes.

Fig. 2 shows the tritium TDS spectra for $Li_{2+x}TiO_3$ measured by PC1. Note that these spectra were obtained by PC1, hence these spectra represent the release behavior of overall tritium. Major tritium release peaks were located around 600 K for all $Li_{2+x}TiO_3$ samples. In addition, tritium release around 450 K was clearly found for $Li_{2.4}TiO_3$. Tritium release peaks around 450 and 600 K were named as Peaks 1 and 2, respectively. It was appeared that fraction

Table 1
Amount and release fraction of bred tritium in 0.3 g of samples.

	$Li_{2.0}TiO_3$	$Li_{2.2}TiO_3$	$Li_{2.4}TiO_3$
Bred T (MBq)	1.4	1.6	1.7
Free T (%)	4	6	9
Reduced T (%)	27	26	25
Oxidized T (%)	69	68	66