Study on the sweep gas chemistry effect on vaporization behavior of Li$_2$TiO$_3$ by means of HT mass spectrometry

Atsushi Suzuki [a,*], Michio Yamawaki [a], Masaru Yasumoto [b], Kenji Yamaguchi [a]

[a] *Nuclear Engineering Research Laboratory, Faculty of Engineering, The University of Tokyo, 2-22, Shirakata-Shirane, Tokai-mura, Ibaraki-ken 319-11, Japan*
[b] *Research Center for Nuclear Science and Technology, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*

Abstract

The vapor pressures in the Li$_2$TiO$_3$–D$_2$–D$_2$O system were measured by means of atmosphere controllable high temperature Knudsen effusion mass spectrometry. The effect of D$_2$ and D$_2$O on vaporization behavior was investigated. The enthalpies of the reactions, Li$_2$TiO$_3$ $\rightleftharpoons$ 2Li + 1/2O$_2$ + TiO$_2$ and Li$_2$TiO$_3$ + D$_2$O $\rightleftharpoons$ 2LiOD + TiO$_2$ were calculated to be 1000.9 ± 32.4 and 449.6 ± 53.5 kJ/mol, respectively. From the results of this study, the maximum allowable temperature with respect to Li transport through the sweep gas in fusion reactor blanket was estimated. © 1997 Elsevier Science B.V.

1. Introduction

Lithium-containing oxide ceramics (Li$_2$O, Li$_4$SiO$_4$, LiAlO$_2$, Li$_2$TiO$_3$, etc.) have been proposed as blanket breeder materials in nuclear fusion reactors. The bred tritium should be extracted efficiently in order to establish the fuel cycle of tritium and an inert sweep gas system has been employed for tritium recovery. For the enhancement of tritium release from the surface of the breeder material, the mixing of hydrogen and/or water vapor to inert sweep gas has been proposed.

Tetenbaum and Johnson studied the effect of water vapor addition on the vaporization behavior of Li$_2$O by means of vapor pressure measurement and reported that water vapor enhances the volatility of Li$_2$O in the form of LiOH(g) [1]. Recently, it was observed that D$_2$ and D$_2$O enhance the volatility of Li$_4$SiO$_4$ as Li and LiOD, respectively, by means of Knudsen effusion mass spectroscopy [2,5–7]. Moreover, the effect of H$_2$ or H$_2$O addition on the vaporization behavior of LiAlO$_2$ was investigated with atmosphere controllable high temperature mass spectrometry [8].

In this study, the vapor pressures in the Li$_2$TiO$_3$–D$_2$– D$_2$O system was measured for the first time with an atmosphere controllable high temperature mass spectrometer and the maximum allowable temperature with respect to the Li transport through the sweep gas in the fusion reactor blanket was estimated.

2. Experimental

The atmosphere controllable high temperature mass spectrometer developed in our earlier work [6] was modified so as to make vapor pressure measurements at higher temperatures up to ∼ 1800 K [8]. The important feature of this system was that the gas inlet system was connected to the Knudsen cell to allow simulated sweep gas containing either D$_2$ or D$_2$O to come into the cell.

The Knudsen cell was made of platinum. The cell had an outer diameter of 12.7 mm and an outer height of 25.3 mm. The diameter of the orifice of the cell is 0.5 mm.

The powdered sample of Li$_2$TiO$_3$, which was supplied from Commissariat à l'Energie Atomique, France, was put into the cell and kept under vacuum at 773 K for 5 h.

The partial pressure p_i of species i was evaluated from the ion intensity I_i by using the following equation:

$$p_i = \frac{kI_iT}{\sigma_i\gamma_in_i}, \tag{1}$$

* Corresponding author. Tel.: +81-29 287 8434; fax: +81-29 287 8488; e-mail: atsushi@tokai.t.u-tokyo.ac.jp.

where k, T, σ_i, γ_i and n_i are the device constant, temperature, ionization cross-section, gain of the electron multiplier and isotopic abundance ratio of species i, respectively. The device constant k was obtained from the consumed quantity, Q, of Ar gas and the conductance of the orifice of the Knudsen cell. When the decrease of Ar pressure in the chamber of Ar supply at the time interval of Δt is ΔP, Q can be expressed as follows:

$$Q = \frac{\Delta P \times V}{\Delta t}, \qquad (2)$$

where V is the inner volume of the chamber. On the other hand, Q can be expressed as follows, using the conductance of the orifice of the Knudsen cell, C:

$$Q\frac{T_{cell}}{T_{out}} = C(P_\in - P_{out}), \qquad (3)$$

where T_{cell} and T_{out} are the inner and outer temperatures of the Knudsen cell, respectively. P_{in} and P_{out} are the pressure inside and outside of the cell, respectively. C can be calculated from the shape of the orifice. Assuming that P_{out} is negligible compared with P_{in} ($\Delta P \sim P_{in}$), the device constant k can be expressed as follows:

$$k = \frac{P_{in}\sigma\gamma n}{IT}. \qquad (4)$$

Ionizing electrons were accelerated to 30 eV. The ionization cross-sections of atoms were obtained from Mann's data [3] and those of molecules were calculated by a method of Kordis and Gingerich [4].

Three runs were performed in the temperature range of 1373–1573 K. In run 0, no sweep gas was introduced to the cell; in run 1 and run 2, D_2 and D_2O were introduced, respectively. Prior to each run, the Li_2TiO_3 sample was kept in vacuum at 573 K for about 10 h.

3. Results and discussion

3.1. Vaporization behavior in Li_2TiO_3–D_2–D_2O system

The vapor pressures over Li_2TiO_3 were measured in run 0. The detected species were Li and Li_2O. The partial pressures of these species are shown in Fig. 1 as a function of temperature. And the resulting equations are as follows:

$$\log P_{Li} = -19.17 \pm 0.59 \times \frac{1000}{T} + 11.79 \pm 0.37, \qquad (5)$$

$$\log P_{Li_2O} = -21.40 \pm 5.64 \times \frac{1000}{T} + 17.47 \pm 3.48. \qquad (6)$$

As seen in Fig. 1, we obtained good agreement between the data in this study and that by Nakagawa et al. [9].
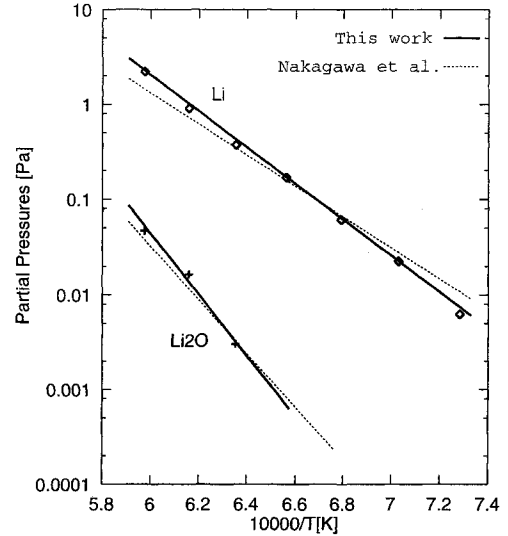

Fig. 1. Partial pressures of vapor species over Li_2TiO_3 (run 0).

In run 1, D_2 was introduced to Li_2TiO_3 and the detected vapor species were Li, LiOD, Li_2O, LiO, D_2O and D_2. Fig. 2 shows the temperature dependence of the partial pressures of these species. The temperature dependence equations of the partial pressures are as follows:

$$\log P_{Li} = -14.31 \pm 1.13 \times \frac{1000}{T} + 9.02 \pm 0.75, \qquad (7)$$

$$\log P_{LiOD} = -12.01 \pm 1.36 \times \frac{1000}{T} + 7.31 \pm 0.90, \qquad (8)$$

$$\log P_{Li_2O} = -36.58 \pm 5.20 \times \frac{1000}{T} + 20.31 \pm 3.19, \qquad (9)$$

$$\log P_{LiO} = -21.77 \pm 1.24 \times \frac{1000}{T} + 10.89 \pm 0.77, \qquad (10)$$

$$\log P_{D_2O} = 4.36 \pm 2.14 \times \frac{1000}{T} - 3.20 \pm 1.42, \qquad (11)$$

$$\log P_{D_2} = 5.44 \pm 2.21 \times \frac{1000}{T} - 3.98 \pm 1.47. \qquad (12)$$

Compared with the data in run 0, it is seen that the vaporization of Li was enhanced by the introduction of D_2 and LiOD was formed by the reaction between Li_2TiO_3 and D_2O, which was formed by oxidation of introduced D_2.

In run 2, D_2O was introduced and Li, LiOD, Li_2O, LiO, D_2O and D_2 were detected. The partial pressures as
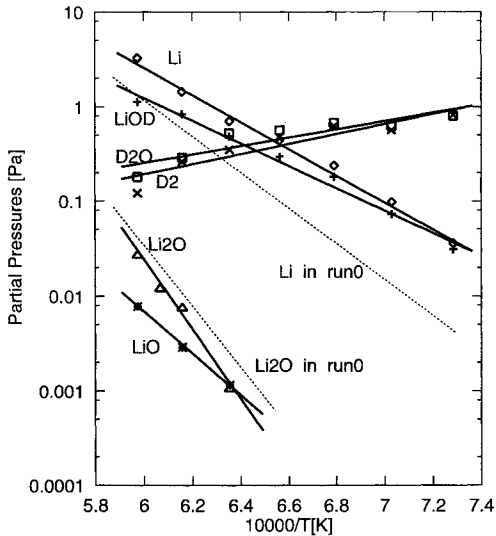
Fig. 2. Partial pressures in the system of D_2–Li_2TiO_3 (run 1).

functions of temperature were shown in Fig. 3. The partial pressure equations were as follows:

$$\log P_{Li} = -16.97 \pm 0.75 \times \frac{1000}{T} + 10.35 \pm 0.49, \quad (13)$$

$$\log P_{LiOD} = -9.01 \pm 1.65 \times \frac{1000}{T} + 5.26 \pm 1.06, \quad (14)$$

$$\log P_{Li_2O} = -28.26 \pm 3.60 \times \frac{1000}{T} + 15.17 \pm 2.21, \quad (15)$$

$$\log P_{LiO} = -27.88 \pm 7.75 \times \frac{1000}{T} + 14.56 \pm 4.76, \quad (16)$$

$$\log P_{D_2O} = 0.639 \pm 0.46 \times \frac{1000}{T} - 4.88 \pm 3.14, \quad (17)$$

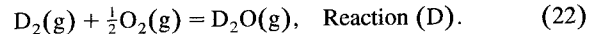$$\log P_{D_2} = 0.149 \pm 0.067 \times \frac{1000}{T} - 1.87 \pm 0.47. \quad (18)$$
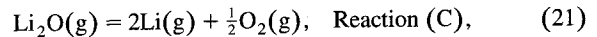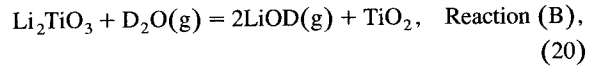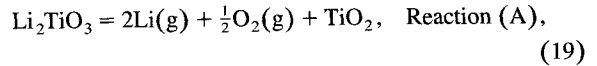
It was seen that LiOD was formed and the vaporization of Li was enhanced by D_2 which was formed by the decomposition of introduced D_2O.

The stated errors (99% confidence level) were derived from an analysis of variance.

3.2. Enthalpies of reactions in Li_2TiO_3–D_2–D_2O system

In the Li_2O–TiO_2 system, four compounds, Li_4TiO_4, Li_2TiO_3, $Li_4Ti_5O_{12}$ and $Li_2Ti_3O_7$, are known [9]. In this study, the measurements were performed in the temperature range 1373–1573 K, while $Li_4Ti_5O_{12}$ is stable only below 1288 K. X-ray diffraction analysis were carried out on the sample before and after the series of the experiment.

The obtained X-ray pattern showed that the near-surface portion of the sample after the experiment was TiO_2 rich. From these facts, the following reactions were considered to take part in the system:

$$Li_2TiO_3 = 2Li(g) + \tfrac{1}{2}O_2(g) + TiO_2, \quad \text{Reaction (A)}, \quad (19)$$

$$Li_2TiO_3 + D_2O(g) = 2LiOD(g) + TiO_2, \quad \text{Reaction (B)}, \quad (20)$$

$$Li_2O(g) = 2Li(g) + \tfrac{1}{2}O_2(g), \quad \text{Reaction (C)}, \quad (21)$$

$$D_2(g) + \tfrac{1}{2}O_2(g) = D_2O(g), \quad \text{Reaction (D)}. \quad (22)$$

However, we could not deny the possibility of formation of $Li_2Ti_3O_7$, as the X-ray pattern for Li_2TiO_3 and $Li_2Ti_3O_7$ are similar and the intensity of the X-ray diffraction for the sample after experiment was considerably small because of difficulty to peel it off from the crucible. Under the assumption of $Li_2Ti_3O_7$ as the residue, another process which produces LiOD can be considered as follows:

$$3Li_2TiO_3 + 2D_2(g) = 2LiOD(g) + 2LiD(g) + Li_2Ti_3O_7,$$
$$\text{Reaction (E)}. \quad (23)$$
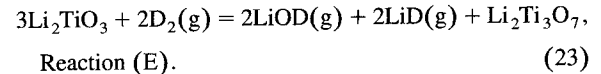
In order to confirm the reliability of the measured partial pressures, third law enthalpies of Eqs. (19) and (20) were calculated. Using the free energy function at temperature of T, (fef(T)), $\Delta H^0(298)$ is given as follows:

$$\Delta H^0(298) = T[-R \ln K - \Delta\text{fef}(T)], \quad (24)$$

where K is the equilibrium constant of the reaction. The values of K for Eqs. (19) and (20) were obtained from the experimental results and the value of the fef were obtained from JANAF thermochemical tables [10]. The calculated
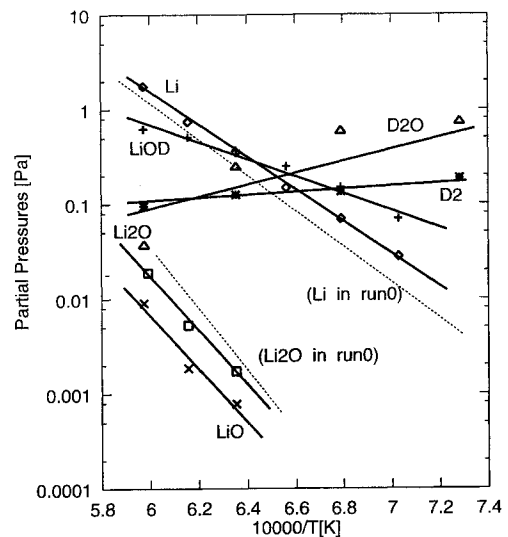

Fig. 3. Partial pressures in the system of D_2O–Li_2TiO_3 (run 2).

Table 1
3rd law ΔH_{298}^0 of Eq. (19) (kJ/mol)

	Run 1	Run 2	Literature
ΔH_{298}^0	975.0 ± 43.5	1026.8 ± 48.1	1050.6 ± 1.5

Table 2
3rd law ΔH_{298}^0 of Eq. (20) (kJ/mol)

	Run 1	Run 2	Literature
ΔH_{298}^0	456.33 ± 55.1	442.8 ± 91.7	505.17 ± 5.7

$\Delta H^0(298)$ for Eqs. (19) and (20) were tabulated in Tables 1 and 2. The differences of $\Delta H^0(298)$ among the runs were smaller than the stated errors. The data from the literature in Tables 1 and 2 were obtained from the calculation [10].

3.3. Discussion on Li loss

In the blanket designs of nuclear fusion reactors, the sum of the pressures of Li-containing species (P_{Li}^{total}) is recommended to be less than 0.01 Pa with respect to Li transport in the sweep gas. In our earlier work, the temperature, T_{max}, at which P_{Li}^{total} reaches 0.01 Pa was estimated for LiAlO$_2$ [8]. In this study, T_{max} was defined as follows:

$$P_{Li}^{total} \ (\text{at } T_{max}) = 0.01 \text{ Pa}, \tag{25}$$

$$P_{Li}^{total} = P_{Li} + P_{LiOD} + P_{Li_2O} + P_{LiO}. \tag{26}$$

The partial pressures of Li containing species can be calculated from the equilibrium constants of Eqs. (19)–(22)

Fig. 4. Temperature at which the sum of the partial pressures of Li-containing species reaches 0.01 Pa.

when the partial pressures of D$_2$ and D$_2$O are given. Since LiD was not detected in this study, it was not Eq. (23) but Eq. (20) that was used for the estimation of the contribution from LiOD. Fig. 4 shows the relation between T_{max} and D$_2$O pressure for D$_2$ pressures of 10, 100 and 1000 Pa, which correspond to a concentration of 0.01, 0.1 and 1% of 1 atm, respectively. The dashed lines in Fig. 4 shows those for LiAlO$_2$ [8] and Li$_4$SiO$_4$ [6]. According to Fig. 4, in order to allow the temperature of the fusion reactor blanket to get to 1000 K, D$_2$O pressure should be controlled to be 0.01 ~ 10 Pa, 0.1 ~ 10 Pa and 1 ~ 10 Pa, for D$_2$ pressure of 10, 100 and 1000 Pa, respectively.

It is considered that, under neutron irradiation, transmutation of Li to tritium takes part in as the competitive process with vaporization. By this process, Li loss is considered to be suppressed and T_{max} may be higher than those estimated here. Moreover, some of the vaporized LiOH are considered to be LiOT under irradiation. The distribution of tritium to several chemical forms was calculated in the previous study [11].

4. Conclusion

The vaporization behavior of Li$_2$TiO$_3$ under the flow of D$_2$ or D$_2$O was studied by means of the atmosphere controllable high temperature mass spectrometry. From the estimated maximum allowable temperature with respect to Li transport through the sweep gas, it was considered that when the partial pressure of D$_2$ is 100 Pa, D$_2$O pressure should be controlled to be 0.1 ~ 10 Pa.

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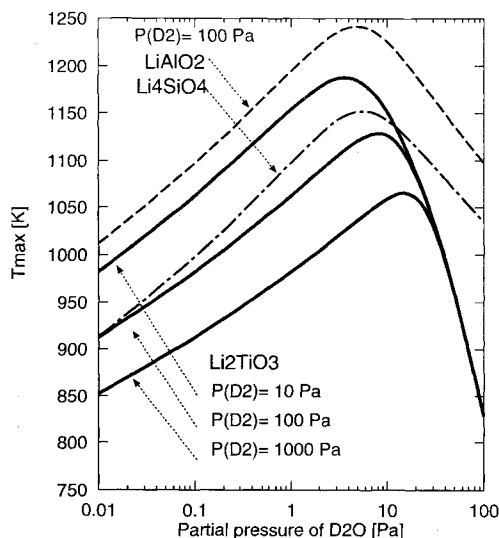[7] H.R. Ihle, R.-D. Penzhorn, P. Schuster, SOFT Conf, Rome, Italy, Sept. 1992.

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