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Sweep gas chemistry effect on lithium transport from ceramic breeder blanket materials

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Abstract

An 'atmosphere controllable high temperature mass spectrometer' was developed in order to investigate the effect of D_2 and/or D_2O on vaporization behavior of ceramic breeder blanket materials. The measurements were made on Li_4SiO_4, $LiAlO_2$ and Li_2TiO_3. The enhancement of Li vaporization and the formation of LiOD caused by D_2 and D_2O introduction, respectively, were confirmed quantitatively. From the resulting thermodynamic data, an discussion on Li loss from the breeder ceramic materials was made. The maximum allowable temperature with respect to lithium transport through the sweep gas in fusion reactor blanket was estimated. © 1997 Elsevier Science B.V.

1. Introduction

Various lithium-containing ternary oxides are proposed as tritium breeder materials in blanket designs of the nuclear fusion reactors [1].

In design of the tritium breeder blanket, the vaporization behavior of the candidate ceramic breeder is one of its important properties. The partial pressures over Li_2O [2–4,7], Li_4SiO_4 [8–10], $LiAlO_2$ [11,12], Li_2TiO_3 [13,20], and other lithium containing ternary oxides have been reported. An inert sweep gas system has been employed for the transportation/recovery of tritium from the surface of breeder materials, and mixing of hydrogen with the inert sweep gas was proposed in order to enhance the release of bred tritium. In such a system, it is important to know the effect of hydrogen and water vapor on vaporization behavior of breeder blanket materials. Recently, sweep gas chemistry of lithium oxide ceramics was studied on Li_4SiO_4 by Ihle et al. [14]. The authors have developed 'atmosphere controllable high temperature mass spectrometry' and studied the vaporization behavior of Li_4SiO_4 [17], $LiAlO_2$ [18] and Li_2TiO_3 [19] under the introduction of D_2 or D_2O.

2. Experimental

Knudsen effusion mass spectrometry is a very useful method to investigate vaporization behavior [15,16]. In order to make measurements under the condition of simulated sweep gas, a gas inlet tube was attached to the Knudsen cell [17], the orifice of which had a diameter of 0.5 mm. The conductance of the tube should be smaller than that of the orifice of the Knudsen cell so as not to destroy the equilibrium condition in the cell. The pressure of the simulated sweep gas in the Knudsen cell was determined from the conductance of the gas inlet tube and the initial pressure of the sweep gas. However, when the temperature of the Knudsen cell was increased, the top portion of the tube was heated so high that the apparent conductance of the tube appeared to have been reduced significantly. Therefore, it was not possible to maintain constant pressure in the cell in the temperature range higher than ~ 1350 K. In order to control the pressure in the cell, the gas inlet system was modified such as shown in Fig. 1. The system consists of a gas inlet Pt tube (0.6 mm diameter × 220 mm length) in the mass spectrometer and a capillary tube (0.2 mm diameter × 600 mm length) outside of the mass spectrometer. The conductance of the gas inlet tube was larger than that of the capillary tube so that the total conductance of the gas inlet system was determined by that of the capillary tube outside of the

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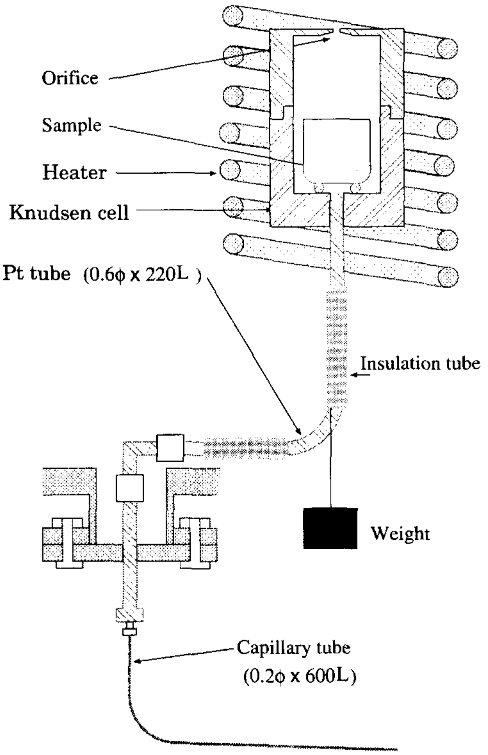

Fig. 1. Schematic drawing of the Knudsen cell with modified gas inlet system.

mass spectrometer. The temperature of the capillary tube was little affected by the heated Knudsen cell. Consequently, this modification allowed the pressure of the sweep gas (D_2) in the cell to be controlled at much higher temperatures. Fig. 2 shows the pressures of the introduced gases (Ar, He and D_2) in the cell. In the case of D_2, which was very important in this study, the pressure (P_{D_2}) was kept to be constant in the temperature range < 1550 K. In the vapor pressure measurements, P_{D_2} can be considered to be constant within a few factor up to ~ 1750 K.

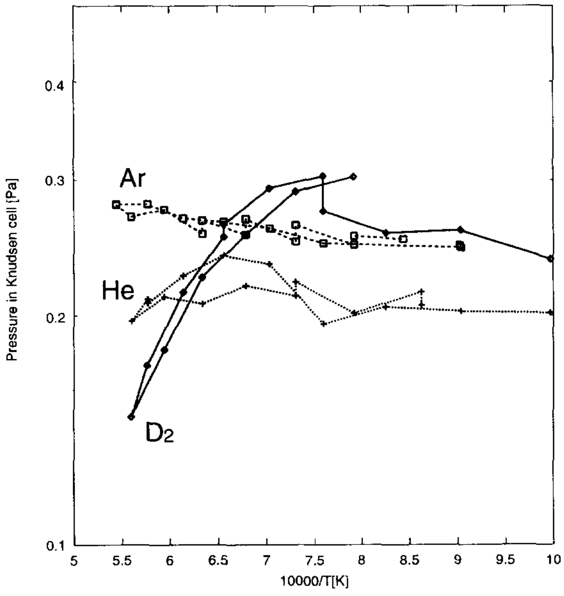

Fig. 2. Temperature dependence of the pressure of introduced D_2, He and Ar.

Ionizing electrons were accelerated to 30 eV. The ionization cross-sections of atoms were obtained from Mann's data [5] and those of molecules were calculated by a method of Kordis and Gingerich [6].

The powdered sample held in a small Pt crucible was installed in a Pt Knudsen cell. The D_2 and D_2O gases were used instead of the H_2 and H_2O gases because of the large background at mass 18.

3. Vaporization behavior of lithium oxide ceramics under condition of sweep gas introduction

3.1. Li_4SiO_4

Gas/solid equilibria for the Li_4SiO_4 system was investigated in the temperature range of 1223–1423 K. The Li_4SiO_4 sample was prepared by Mitsubishi Material and supplied to the authors by courtesy of the Japan Atomic Energy Research Institute. In this experiment, four runs were performed (run0–run3). Prior to each run, except for run3, the sample was kept in vacuum for 4 h at 723 K for outgassing. The system was calibrated by measuring the intensity of $^{107}Ag^+$ ion.

In run0, no gas was introduced, and Li was observed as the primary vapor species in the temperature range described above. In run1 and run2, D_2 and D_2O were introduced, respectively. The detected vapor species were

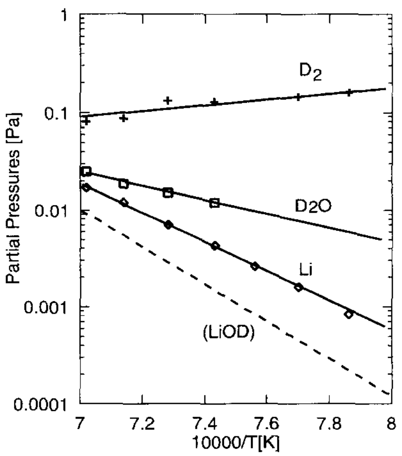

Fig. 3. Partial pressures in the system D_2 /Li_4SiO_4 [17].

Li, D_2 and D_2O in run1, while the enhancement of Li vaporization was confirmed from comparison between the results of run0 and run1. The vapor pressure as a function of temperature in run1 is shown in Fig. 3. In run2, Li, LiOD, D_2 and D_2O were detected. The formation of LiOD from the reaction between D_2O and Li_4SiO_4 was observed. The reactions assumed to take place in the Li_4SiO_4–D_2, D_2O systems are as follows:

$$Li_4SiO_4(s) = 2Li(g) + \tfrac{1}{2}O_2(g) + Li_2SiO_3(s), \quad (1)$$

$$Li_4SiO_4(s) + D_2O(g) = 2LiOD(g) + Li_2SiO_3(g). \quad (2)$$

The equilibrium constants for Eqs. (1) and (2), K_A and K_B, could be calculated from the experimental results of run1 and run2, under the assumption that the activities of the condensed phases are unity or cancel each other. The calculated K_A and K_B differed run by run. This difference was attributed to be non-stoichiometry of Li_4SiO_4, such as Li_4SiO_{4-x}, after speculation by Ihle et al. [14]. They proposed the non-stoichiometric composition of Li_4SiO_{4-x} to be formed by the following reaction:

$$Li_4SiO_4 + xD_2 \rightleftharpoons xD_2O + Li_4SiO_{4-x}. \quad (3)$$

In order to discuss the potential for non-stoichiometry, run3 was carried out with D_2 introduced. The sample in run3 had been exposed to D_2O in run2, while the baking treatment was not performed prior to run3. Accordingly, the Li_4SiO_4 sample was considered to have attained a more oxidized state in run3 than in run1. This assumption was supported by comparing the oxygen partial pressure in each run. The relative order of x in each run can be expressed according to the value of oxygen partial pressure as follows:

$$x(\text{run1}) > x(\text{run3}) > x(\text{run2}). \quad (4)$$

From the data, K_A and K_B, become smaller as x becomes larger on taking into account of Eq. (3), x of each run can be estimated to follow the order shown in Eq. (4). Actually, K_A and K_B became smaller as Li_4SiO_4 was conditioned to a more reduced state.

Table 1
3rd law ΔH°_{298} of Eqs. (5) and (6) (kJ/mol) (1600 K) [18]

	ΔH°_{298} (Eq. (5))	ΔH°_{298} (Eq. (6))
run4	2044.3 ± 81.0	
run5	2010.3 ± 122.7	925.3 ± 137.6
run6	2028.2 ± 243.3	935.4 ± 164.1

3.2. $LiAlO_2$

For measurement of vapor pressures in the $LiAlO_2$–D_2–D_2O system, a higher temperature range, such as ~ 1700 K, needed to be attained. The measurement of this system was actually carried out in the temperature range of 1573–1773 K. Three measurements (run4–run6) were made. The conventional $^{107}Ag^+$ method was used for the calibration of the mass spectrometer. Run4 was carried out with no gas introduction, and Li and O_2 were detected as the vapor species. The temperature dependence of these species had good agreement with those reported by Ikeda et al. [12]. In run5, D_2 was introduced, and Li, LiOD, O_2, D_2 and D_2O gaseous species were observed. The enhancement of Li vaporization was observed, which can be explained from the fact that the partial pressure of O_2 was smaller and the partial pressure of Li was larger in run5 than in run4 (Fig. 4). In run6, D_2O at an average partial pressure of 2.0×10^{-2} Pa, was introduced. The observed gaseous species were Li, LiOD, O_2 and D_2O; the amount of D_2 was too small to be detected. In $LiAlO_2$–D_2–D_2O

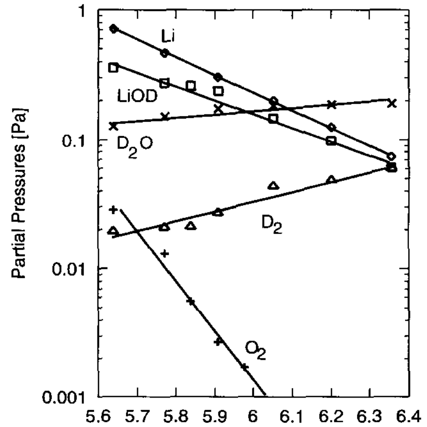

Fig. 4. Partial pressures in the system D_2 /$LiAlO_2$ [18].

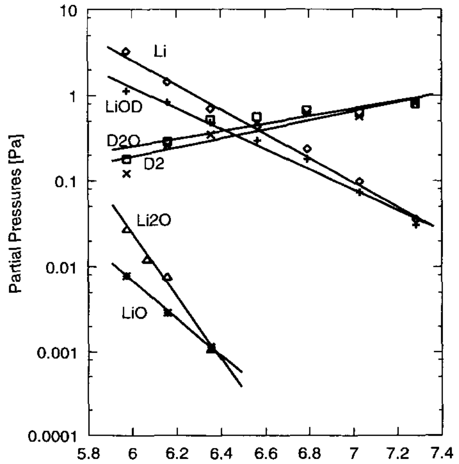

Fig. 5. Partial pressures in the system D_2 /Li_2TiO_3 [19].

Table 2
3rd law ΔH°_{298} (Eq. (7)) and ΔH°_{298} (Eq. (8)) (kJ/mol) (1500 K) [19]

	ΔH°_{298} (Eq. (7))	ΔH°_{298} (Eq. (8))
run8	975.0 ± 43.5	456 ± 55.1
run9	1026.8 ± 48.1	442.8 ± 91.7
Literature	1050.6 ± 1.5	505.17 ± 5.7

system, the equilibrium was considered to be established according to the following reactions:

$$5\mathrm{LiAlO_2(s)} = 4\mathrm{Li(g)} + \mathrm{O_2(g)} + \mathrm{LiAl_5O_8(s)}, \qquad (5)$$

$$5\mathrm{LiAlO_2(s)} + 2\mathrm{D_2O(g)} = 4\mathrm{LiOD(g)} + \mathrm{LiAl_5O_8(s)}. \qquad (6)$$

Any significant differences in either the equilibrium constants or the standard enthalpies, ΔH°_{298}, of the Eqs. (5) and (6) were not recognized among the runs. The third law ΔH°_{298} of Eqs. (5) and (6) are tabulated in Table 1. The differences of ΔH°_{298} among the three runs are smaller than the stated errors.

3.3. Li_2TiO_3

The vapor pressures for the Li_2TiO_3–D_2–D_2O system were measured in the temperature range of 1373–1673 K. The sample of Li_2TiO_3 was supplied by courtesy of Dr. Roux of Commissariat à l'Energie Atomique. Three runs, run7 with no gas introduced, run8 with D_2 introduced, and run9 with D_2O introduced, were performed. In run7, Li and Li_2O were detected. In run8 and run9, Li, LiOD, Li_2O, LiO, D_2O and D_2 were detected. Fig. 5 shows the partial pressures as a function of inverse temperature of the species detected in run8. The enhancement of Li vaporization due to D_2 introduction and the formation of LiOD caused by D_2O introduction were confirmed from the results of run8 and run9, respectively. The following reactions were considered to take part in the system:

$$\mathrm{Li_2TiO_3(s)} = 2\mathrm{Li(g)} + \tfrac{1}{2}\mathrm{O_2(g)} + \mathrm{TiO_2(s)}, \qquad (7)$$

$$\mathrm{Li_2TiO_3(s)} + \mathrm{D_2O(g)} = 2\mathrm{LiOD(g)} + \mathrm{TiO_2(s)}, \qquad (8)$$

$$\mathrm{Li_2O(g)} = 2\mathrm{Li(g)} + \tfrac{1}{2}\mathrm{O_2(g)}. \qquad (9)$$

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 [20]. In this study, the measurements were performed in the temperature range of 1373 K–1573 K, while $Li_4Ti_5O_{12}$ is stable only below 1288 K. These facts mean that Li_2TiO_3 was vaporized as Li and O_2, making Li_2TiO_3 sample to be TiO_2 rich. The third law $\Delta H^\circ(298)$ for the Eqs. (7) and (8) were calculated and tabulated in Table 2. The equilibrium constants of Eqs. (7) and (8) were obtained from the experimental results tabulated in Table 3, and the value of Gibbs free energy function (fef) were obtained from JANAF Thermochemical Tables [21]. The differences of $\Delta H^\circ(298)$ among the runs were smaller than the stated errors.

4. Discussion on Li-loss

In the blanket designs, the sum of the partial pressures of Li-containing species ($P_{\mathrm{Li}}^{\mathrm{total}}$) has been recommended to be 0.01 Pa [14] as the maximum pressure with respect to Li transport through the sweep gas. We estimated the temperature at which $P_{\mathrm{Li}}^{\mathrm{total}}$ reaches 0.01 Pa. We defined $T_{\max}$ as follows:

$$P_{\mathrm{Li}}^{\mathrm{total}}(\text{at } T_{\max}) = 0.01 \text{ (Pa)}, \qquad (10)$$

$$P_{\mathrm{Li}}^{\mathrm{total}} = \sum_i P_i, \ (i\text{: Li containing species}). \qquad (11)$$

Li containing species were Li and LiOD in the results for Li_4SiO_4 and $LiAlO_2$, and Li, LiOD, Li_2O and LiO in the results for Li_2TiO_3. P_i can be calculated from the equilibrium constants of Eqs. (1), (2), (5)–(8), as well as $D_2 + 1/2O_2 = D_2O$ when P_{D_2} and P_{D_2O} are given. Fig. 6(a)–(c) show $T_{\max}$ calculated for Li_4SiO_4, $LiAlO_2$ and Li_2TiO_3 from the experimental results. And Fig. 6(d) shows $T_{\max}$

Table 3
The temperature dependence of the partial pressures of detected species in run8 and run9. $\log P_i = a \times 1000/T + b$ [19]

	run8		run9	
	a	b	a	b
$\log P_{\mathrm{Li}}$	−14.31 ± 1.13	9.02 ± 0.75	−16.97 ± 0.75	10.35 ± 0.49
$\log P_{\mathrm{LiOD}}$	−12.01 ± 1.36	7.31 ± 0.93	−9.01 ± 1.65	5.26 ± 1.06
$\log P_{\mathrm{Li_2O}}$	−36.58 ± 5.20	20.31 ± 3.19	−28.26 ± 3.61	15.17 ± 2.21
$\log P_{\mathrm{LiO}}$	−21.77 ± 1.24	10.89 ± 0.77	−27.88 ± 7.75	14.56 ± 4.76
$\log P_{\mathrm{D_2O}}$	4.36 ± 2.14	−3.20 ± 1.42	0.639 ± 0.46	−4.88 ± 3.14
$\log P_{\mathrm{D_2}}$	5.44 ± 2.21	−3.98 ± 1.47	0.149 ± .0.067	−1.87 ± 0.46

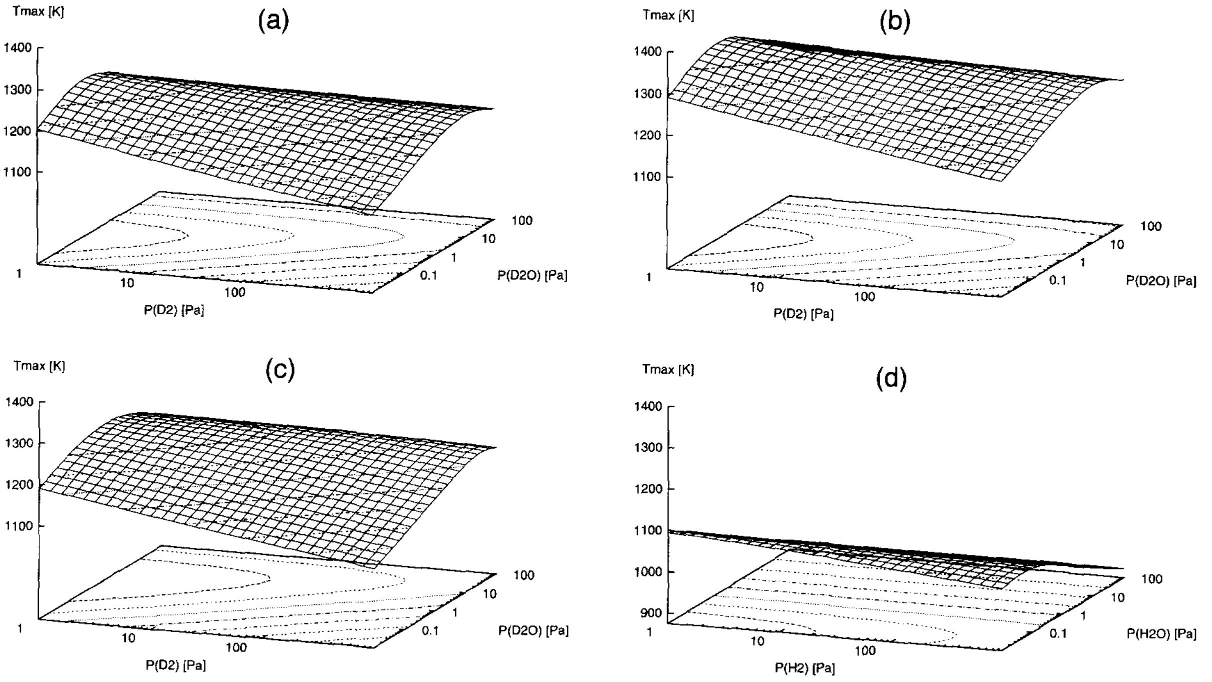

Fig. 6. Temperature at which the sum of the partial pressure of Li-containing species reaches 0.01 Pa. (a) Li_4SiO_4, (b) $LiAlO_2$, (c) Li_2TiO_3, (d) Li_2O.

for Li_2O calculated from literature [21]. The range of P_{D_2} and P_{D_2O} are [1, 1000 Pa] and [0.01, 100 Pa], respectively. Fig. 7 shows T_{max} at $P_{D_2} = 100$ Pa (i.e., 0.1%). It was considered that when 0.1% hydrogen is mixed to inert sweep gas, Li_2TiO_3 is compatible to Li_4SiO_4 with respect to Li loss.

Under neutron irradiation, transmutation of Li 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 [22].

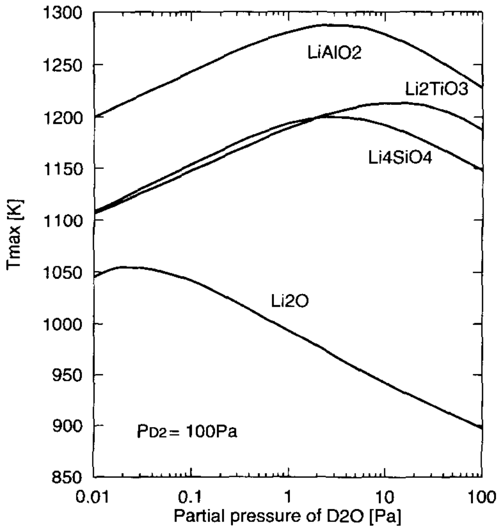

Fig. 7. T_{max} at $P_{D_2} = 100$ Pa (0.1%).

5. Summary

A Knudsen effusion mass spectrometer which is capable of introducing simulated sweep gases into a Knudsen cell has been established, and a gas inlet system has been incorporated so as to allow the pressure of the introduced gas in the Knudsen cell to be controlled at a higher temperature (up to 1750 K). By using the 'atmosphere controlled high temperature mass spectrometer', so called here, the vaporization behavior of Li_4SiO_4, $LiAlO_2$ and Li_2TiO_3 under the introduction of D_2 or D_2O were studied. From the resulting thermodynamic data, the maximum allowable temperatures with respect to Li transport through the sweep gas in the blanket of fusion reactors were estimated.

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