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Sweep gas chemistry effect on vaporization property of Li_2ZrO_3

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Abstract

The equilibrium vapor pressures in the system of Li_2ZrO_3–D_2 were measured by means of atmosphere controlled high temperature mass spectrometry. The effect of D_2 on vaporization of lithium containing species was investigated quantitatively. The sum of the partial pressures of lithium containing species was estimated to be approximately 0.002 Pa at 1000 K under the condition of 0.1% hydrogen addition into the helium purge gas. The standard enthalpies of the reactions in this system were calculated from the experimental data, which suggested a possibility of non-stoichiometric composition in the surface region of Li_2ZrO_3.

1. Introduction

On designing the tritium breeder blanket for fusion reactors, the vaporization behavior of the breeders is among the essential characteristics to be evaluated for assessing their performance. The mixing of hydrogen with the inert sweep gas has been employed for enhancement of the tritium release rate from the breeder materials. It is valuable to clarify the effect of hydrogen and moisture on the vaporization behavior.

The effect of water vapor addition on the vaporization behavior of Li_2O was first investigated by Tetenbaum and Johnson [1] by means of vapor pressure measurements, and the enhancement of the volatility of Li_2O in the form of LiOH was reported. The effect of hydrogen and/or water vapor addition on vaporization of lithium containing species from Li_4SiO_4 [2–5], $LiAlO_2$ [6], Li_2TiO_3 [7] has been studied by means of mass spectrometry and the enhancement of volatility was observed.

Penzhorn et al. [2] has pointed out that an oxygen deficient layer might be formed near the surface by a reaction of hydrogen with oxygen from Li_4SiO_4. The authors have also observed differences in the enthalpies of vaporization reactions of Li_4SiO_4 depending on its history, which was related to the formation of a non-stoichiometric layer near its surface [4]. Kawamura et al. [8] reported a possibility of non-stoichiometry in Li_2ZrO_3 based on the measurement of the amount of water generated in a Li_2ZrO_3 bed with hydrogen addition to the sweep gas.

In this study, the vapor pressures of lithium containing species over Li_2ZrO_3 with D_2 addition were measured using atmosphere controlled high temperature mass spectrometry. The enhancement of vaporization of the Li containing species and the possibility of non-stoichiometric layer formation are discussed.

2. Experimental

The atmosphere controllable high temperature mass spectrometer developed in the author's earlier works allows one to make a vapor pressure measurement at

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high temperatures up to approximately 1800 K with low pressure gas addition [6].

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 was 0.5 mm. Low pressure D_2 gas was introduced to the cell through the gas inlet tube, whose conductance was set to be smaller than that of the orifice of the cell so as not to destroy the equilibrium in the cell.

The sample of Li_2ZrO_3 was supplied by CEA, Saclay, France. The powdered sample was put into the cell and kept in vacuum at 773 K for approximately 5 h in order to remove LiOH which has been formed at the surface due to the reaction with the atmosphere.

The partial pressure of species i, P_i, was evaluated from the current intensity, I_i, by using the following equation,

$$P_i = \frac{kI_iT}{\sigma_i\gamma_i n_i w_i}, \tag{1}$$

where k, T, σ_i, γ_i and n_i are the device constant, temperature, ionization cross section, gain of the electron multiplier and isotope abundance ratio of species i, respectively. The device constant k was obtained by measuring the intensity of $^{107}Ag^+$ ion. Ionizing electrons were accelerated to 30 eV. The factor of w_i is the ionization efficiency at 30 eV obtained from the ionization efficiency curves [9]. The ionization cross sections of atoms were obtained from Mann's data [10] and those of molecules were calculated with the method described by Kordis and Gingerich [11].

3. Results and discussion

Two different runs of measurement, run 1 and 2, were performed in the temperature range of 1473–1673 K. The partial pressures of the vaporized species were measured without sweep gas in run 1 and with D_2 introduced in run 2.

3.1. Vaporization behavior in Li_2ZrO_3–D_2 system

The detected species in run 1 were Li, O_2, Li_2O and LiO. The partial pressures of these species are shown in Fig. 1 as a function of temperature. The resulting equations obtained from the least squares method were as follows:

$$\log P_{\mathrm{Li}} = (-19.41 \pm 0.40) \times \frac{1000}{T} + 11.36 \pm 0.26, \tag{2}$$

$$\log P_{\mathrm{O_2}} = (-21.79 \pm 0.51) \times \frac{1000}{T} + 12.18 \pm 0.32, \tag{3}$$

$$\log P_{\mathrm{Li_2O}} = (-26.08 \pm 0.58) \times \frac{1000}{T} + 13.76 \pm 0.36, \tag{4}$$

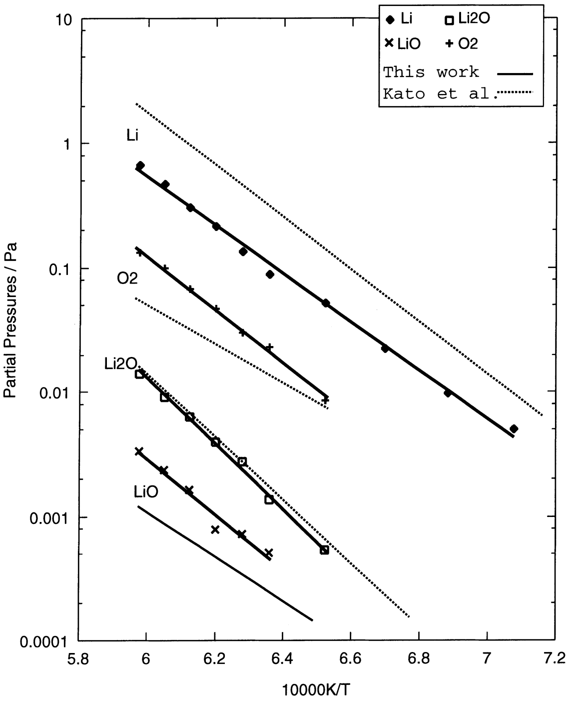

Fig. 1. Partial pressures of vapor species over Li_2ZrO_3 (run 1).

$$\log P_{\mathrm{LiO}} = (-22.42 \pm 1.72) \times \frac{1000}{T} + 10.93 \pm 1.06. \tag{5}$$

The dotted lines in Fig. 1 show the data by Kato et al. [12]. The oxygen partial pressure in the present work was larger than that of Kato et al., which is considered to have caused the difference of partial pressures of Li and LiO. The partial pressure of Li_2O is not considered to depend on the oxygen potential as seen in the following reaction,

$$\mathrm{Li_2ZrO_3(s) = Li_2O(g) + ZrO_2(s)}, \quad \text{Reaction A.} \tag{6}$$

As seen in Fig. 1, good agreement was obtained between $P_{\mathrm{Li_2O}}$ of the present authors and that of Kato et al.

Fig. 2 shows the partial pressures of detected species when D_2 was introduced to Li_2ZrO_3 (run 2). The temperature dependence of the species were as follows.

$$\log P_{\mathrm{Li}} = (-8.50 \pm 0.48) \times \frac{1000}{T} + 5.06 \pm 0.31, \tag{7}$$

$$\log P_{\mathrm{O_2}} = (-45.40 \pm 7.69) \times \frac{1000}{T} + 25.52 \pm 4.65, \tag{8}$$

$$\log P_{\mathrm{Li_2O}} = (-23.56 \pm 0.45) \times \frac{1000}{T} + 12.07 \pm 0.28, \tag{9}$$

$$\log P_{\mathrm{LiO}} = (23.78 \pm 1.44) \times \frac{1000}{T} + 11.52 \pm 0.88, \tag{10}$$

$$\log P_{\mathrm{LiOD}} = (-9.89 \pm 0.58) \times \frac{1000}{T} + 5.42 \pm 0.37, \tag{11}$$

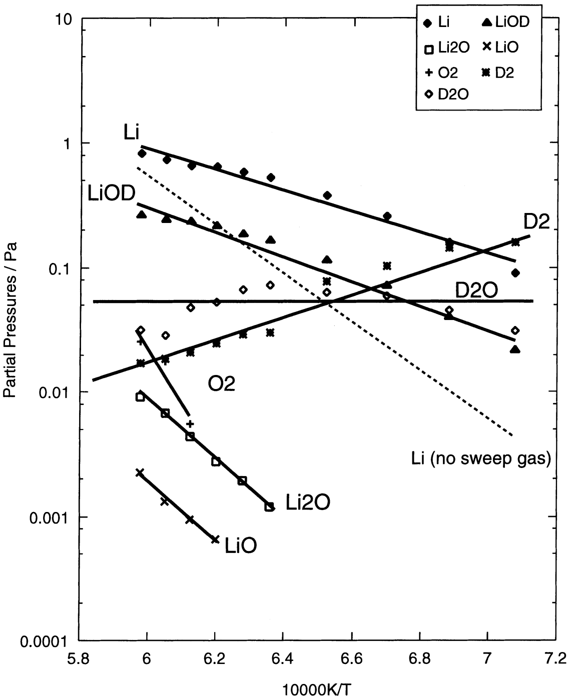

Fig. 2. Partial pressures of vapor species in the system of Li_2ZrO_3–D_2 (run 2).

$$\log P_{D_2O} = (0.17 \pm 1.26) \times \frac{1000}{T} - 1.43 \pm 0.81. \qquad (12)$$

The partial pressure of the introduced D_2 was as follows,

$$\log P_{D_2} = (10.10 \pm 0.68) \times \frac{1000}{T} - 7.84 \pm 0.44. \qquad (13)$$

The dashed lines in Fig. 2 are the data obtained in run 1. X-ray diffraction analyses were carried out on the samples before and after the experiment. The obtained X-ray pattern showed that Li_2ZrO_3(s) and small amount of ZrO_2(s) coexisted in the sample and that the amount of ZrO_2 after the experiment was larger than that before. From these facts, the following reactions were considered in the system of Li_2ZrO_3–D_2,

$$Li_2ZrO_3(s) = 2Li(g) + \tfrac{1}{2}O_2(g) + ZrO_2(s), \quad \text{Reaction B,} \qquad (14)$$

$$Li_2ZrO_3(s) + D_2O(g) = 2LiOD(g) + ZrO_2(s), \quad \text{Reaction C,} \qquad (15)$$

$$Li(g) + LiO(g) = Li_2O(g), \quad \text{Reaction D,} \qquad (16)$$

$$D_2(g) + \tfrac{1}{2}O_2 = D_2O(g), \quad \text{Reaction E.} \qquad (17)$$

D_2 introduction caused the decrease of oxygen potential in the system and Li vaporization was enhanced (Reaction B and E) as seen in Fig. 2. LiOD was formed by the Reaction C. Any significant dependence of Li_2O partial pressure on oxygen potential was not observed.

3.2. Enthalpies of reactions in Li_2ZrO_3–D_2 system

The standard enthalpies (ΔH_r(298 K)) of Reactions A ~ D were calculated using the third law treatment. The free energy functions, *fef*, of the detected species were obtained from JANAF thermochemical tables [13]. Because no *fef* data were available for D_2, D_2O and LiOD, the *fef* data of H_2, H_2O and LiOH were used, respectively. The equilibrium constants of the reactions were obtained from the vapor pressures described above assuming the activities of the condensed phases to be unity. The calculated ΔH_r(298 K) are shown in Table 1. Runs 3 and 4 were performed under the same condition of runs 1 and 2, respectively.

Good agreements among the results of the runs were obtained for ΔH_A(298 K) and ΔH_B(298 K). On the other hand, considerable differences were found in ΔH_D(298 K). The values of ΔH_D(298 K) in runs 2 and 4 were larger than those in runs 1 and 3. It may suggest the existence of oxygen deficient layer at the surface of Li_2ZrO_3. The possibility of the existence of a non-stoichiometric layer at the surface of Li_4SiO_4 had been pointed out based on the vapor pressure measurements [3,4]. It was also reported that Li_2ZrO_3 might have non-stoichiometry [8]. The data of the present work are supporting this hypothesis.

3.3. Enhancement of Li vaporization

The measurements in the present work allow an estimation of lithium loss from the breeder materials. In some designs of the blanket, mixing of 0.1% hydrogen into the sweep gas of 1 atm had been proposed [14]. In

Table 1
ΔH_r (298 K) of reactions A ~ D (kJ/mol)

	Reaction A	Reaction B	Reaction C	Reaction D
Run 1	510.1 ± 0.9	975.0 ± 2.9	–	−388.2 ± 1.9
Run 2	514.3 ± 0.8	973.6 ± 3.2	439.7 ± 1.3	−380.9 ± 4.2
Run 3	512.5 ± 1.0	981.6 ± 5.8	–	−388.5 ± 1.9
Run 4	516.6 ± 1.9	976.6 ± 2.1	444.3 ± 2.0	−383.0 ± 0.4

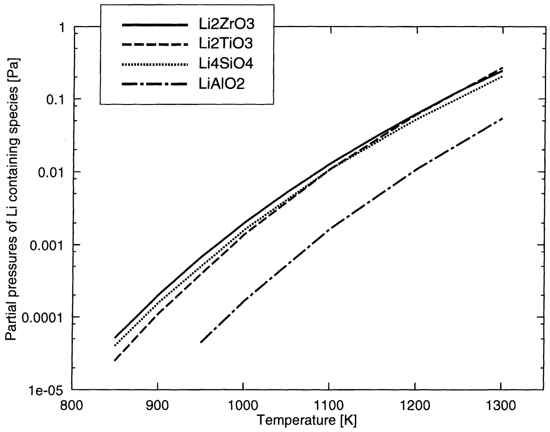

Fig. 3. Summation of the partial pressures of lithium containing species as a function of temperature for Li_2ZrO_3 (this work), Li_4SiO_4, $LiAlO_2$ and Li_2TiO_3.

this paper, the summation of partial pressures of lithium containing species was calculated under a condition of 100 Pa hydrogen addition to the sweep gas. The calculation was carried out under the following assumptions:

1. The number of D atoms in the equilibrated system of Li_2ZrO_3–D_2 is equal to that in the sweep gas at the inlet, i.e.,

$$P_{D_2} + P_{D_2O} + \tfrac{1}{2}P_{LiOD} = 100\ \text{Pa}, \tag{18}$$

   where other D containing species is considered to be negligible since they were not detected in the measurements.
2. The stoichiometric composition is kept in the vaporization, i.e., the ratio between the number of Li atoms and that of O atoms is 2.

$$\frac{P_{Li} + P_{LiOD} + 2P_{Li_2O} + P_{LiO}}{2P_{O_2} + P_{D_2O} + P_{LiOD} + P_{Li_2O} + P_{LiO}} = 2. \tag{19}$$

   The assumption is based on the fact that the residue after the vaporization was ZrO_2.

Using Eqs. (18) and (19) together with the equilibrium constants of Reactions A $\sim$ E obtained from the measurements, the partial pressures of lithium containing species, P_{Li}^{total}, was calculated (Fig. 3). The lines for Li_2TiO_3 [7], $LiAlO_2$ [6] and Li_4SiO_4 [4] were obtained in the same manner by using the data in the previous studies. If the temperature of the blanket is 1000 K, P_{Li}^{total} is approximately 0.002 Pa in the case of Li_2ZrO_3.

4. Conclusion

The vapor pressures in the system of Li_2ZrO_3–D_2 were measured with an atmosphere controllable H-T mass spectrometer. The possibility of the non-stoichiometric layer near the surface of Li_2ZrO_3 was pointed out. The lithium loss was estimated under the condition of 100 Pa hydrogen addition into the sweep gas. Li_2ZrO_3 has comparative characteristics in regard of the Li loss compared with Li_2TiO_3 and Li_4SiO_4.

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