Hydrogen Recovery from Liquid Li with Y Hot Trap[*)]

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Materials to compose a fusion reactor chamber are subjected to neutron irradiation. International Fusion Materials Irradiated Facility (IFMIF) will be used to analyze how neutron damage affects material durability. The material is irradiated by high-intensity neutron beam, which is generated by the D-Li stripping reaction. Tritium (T) generated by by-pass reaction needs to be recovered from liquid Li for safety. Recovery of tritium by an yttrium (Y) hot trap is one of the ways to recover T from liquid Li in IFMIF. Therefore, it is necessary to analyze the behavior of T in the liquid Li. In this study, the authors measured H_2 absorption rates under stirred conditions of liquid Li and analyzed the effect of hydrogen absorption rate of Y by elevating temperature from 250°C to 400°C to establish the way to recover T from liquid Li with the Y hot trap in IFMIF. Judging from the comparison, we considered the rate-determining step is H diffusion in Y. Mass transfer coefficients at each temperature were determined by fitting the results between calculation and experiment.

1. Introduction

The use of D-Li stripping reaction to generate neutron is expected in the International Fusion Materials Irradiation Facility (IFMIF). In the liquid Li target, trace amount of impurities exist, where protium, deuterium, tritium and other species (N, C, O) are included. Tritium is generated by the D-Li reaction, and D in the beam of the reaction is contained in the Li loop. The generating rates of hydrogen isotopes (D, T) in the Li are approximately 5,160 and 7 g/year [1]. These hydrogen isotopes have to be recovered from the liquid Li loop for safety, and the tritium concentration is reduced below 1 wppm [2]. In addition, trace amounts of impurities (N, C, O) are included in the Li loop. N is removed by a Ti-Fe hot trap and C and O are done by a cold trap.

Y hot trap is expected as the effective hydrogen isotopes recovery system in the IFMIF Li loop. The Y hot trap is operated at around 573 K [2], and therefore, it is necessary to analyze the behavior of T in the liquid Li. We have already traced the results under the conditions of static liquid Li and dynamic liquid Li. We concluded those hydrogen absorption rates of Y from liquid Li depended on the surface condition no matter it was static or dynamic [3]. In the previous experiment, we have proved that HF-treatment to remove oxide (Y_2O_3) formed on Y surface is effective to recover H_2 from Li. The HF-treatment technique was applied to T recovery from neutron-irradiated Li, and a very low concentration of T less than 1 wppm was successfully recovered from static Li by HF- treated Y plate.

Li fluid is used in the actual operation of the IFMIF loop and the Y hot trap is used [4]. However, no temperature dependence is clarified on Y trapping under fluidized Li conditions. Therefore, experiment is performed to trace the behavior of H absorption using solid Y and liquid Li under various temperatures. In this paper, we report recovery rates of H, which is determined by fitting among the results of calculation and experiment using Y from liquid Li under mixing conditions.

2. Theory and Analysis

We create a model of H transfer process in the conjugated $Ar+H_2$-Li-Y system as shown in Fig. 1. The H transfer process of (i)+(ii) is described by the following equation:

$$j_{\text{Li}} = k_{\text{comp,gas-Li}} A_{\text{Li}} (C_g - C_{\text{Li}}^*). \tag{1}$$

Here, j_{Li} (mol/s) is a H absorption rate from a gaseous phase to the Li surface, $k_{\text{comp,gas-Li}}$ (m/s) is a composite mass-transfer coefficient, A_{Li} (m^2) is a Li-gas interface area, C_g (mol/m^3) is a H_2 concentration in the bulk gas and C_{Li}^* is a gaseous-phase H_2 concentration in equilibrium with the Li surface one. It is assumed that the outlet concentration is equal to the bulk one, because complete mixing condition is realized in the present system. Since liquid Li is stirred, the two transfer processes of (iii)+(iv) are described by diffusion through a thin liquid film near interfaces between gas and Li. These two processes are described by the mass-transfer coefficient in a similar way
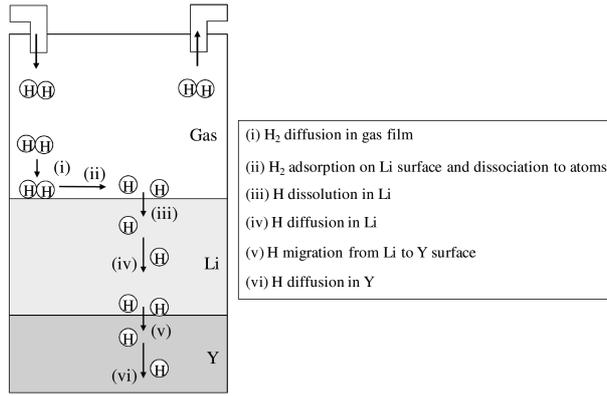
Fig. 1   H transfer processes in the Ar+H$_2$-Li-Y system.

Fig. 2   A schematic diagram of the experiment apparatus.

to Eq. (1). The material balance in the Li layer is described by the following equation:

$$V_{\text{Li}} \frac{\partial C_{\text{Li}}}{\partial t} = j_{\text{Li}} - j_{\text{Li-Y}}. \tag{2}$$

Here, C_{Li} (mol/m^3) is an atomic H concentration dissolved in Li and V_{Li} (m^3) is the volume of Li.

In a similar way to Eq. (1), the process (v) is expressed as follows:

$$j_{\text{Li-Y}} = k_{\text{Li-Y}} A_{\text{Y}} (C_{\text{Li}} - C_{\text{Y}}^*). \tag{3}$$

Here, $j_{\text{Li-Y}}$ (mol/s) is the hydrogen absorption rate from the Li surface to Y, $k_{\text{Li-Y}}$ (m/s) is a mass-transfer coefficient for the process (v), A_{Y} (m^2) is the area of Y, and C_{Y}^* (mol/m^3) is an atomic H concentration on the Y surface.

The process (vi) is described by the one-dimensional diffusion equation of Eq. (4):

$$\frac{\partial C_{\text{Y}}}{\partial t} = D_{\text{Y}} \frac{\partial^2 C_{\text{Y}}}{\partial x^2}, \tag{4}$$

$$t = 0, \ 0 \leq x \leq l_{\text{Y}} : C_{\text{Y}} = 0, \tag{5}$$

$$t > 0, \ x = 0 : -A_{\text{Y}} D_{\text{Y}} \frac{\partial C_{\text{Y}}}{\partial x} = j_{\text{Li-Y}}, \tag{6}$$

$$t > 0, \ x = l_{\text{Y}} : \frac{\partial C_{\text{Y}}}{\partial x} = 0. \tag{7}$$

Here, C_{Y} (mol/m^3) is the H$_2$ concentration in Y, D_{Y} (m^2/s) is the diffusion coefficient of H in Y and l_{Y} (m) is the thickness of Y. We use the value of D_{Y} reported by the reference [5]:

$$\log D_{\text{Y}} = -2.425 - 2402/T. \tag{8}$$

Here, T (K) is absolute temperature. The D_{Y} value at 573 K is 2.41×10^{-11} m^2/s. In addition, equations of equilibrium relation between gas phase and liquid Li, and liquid Li and Y are required. These equations are expressed as follows:

$$C_{\text{Li}} = S_{\text{Li}} \sqrt{P_{\text{H}_2}}, \tag{9}$$

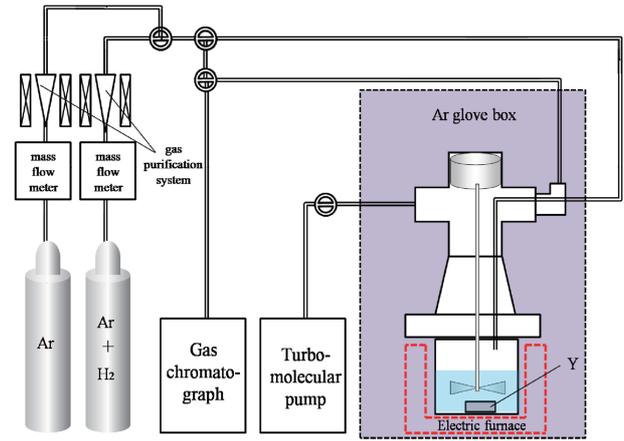$$C_{\text{Y}} = \frac{S_{\text{Y}}}{S_{\text{Li}}} C_{\text{Li}}, \tag{10}$$

Here, S_{Li} ((mol/m^3)/Pa$^{0.5}$) is the solubility of H in Li, S_{Y} is that of H in Y, and P_{H_2} (Pa) is the hydrogen partial pressure. Eq. (10) represents the equilibrium relation between Li and Y.

3. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 2. The reaction vessel, pipes and joints are made of 304 stainless-steel. ST707 SAES getters (Zr-V-Fe alloy) are placed to remove impurities in Ar. A molecular sieve 3A to remove H$_2$O is placed in the H$_2$ gas line. We prepared Li of 99.9% in purity and a Y plate of 99.9% in purity, 0.25 mm in thickness and the rectangular size of 25 mm × 25 mm as experimental samples. Oxide film on the Y surface was removed by HF treatment because the film prevents Y from absorbing H [6, 7]. The Y plate was put in a Mo crucible and Li was put on the plate. In order to keep Li and Y surfaces fresh and clean, all handling is always manipulated in an Ar atmosphere. The Li was stirred by a 316 stainless-steel paddle blade with 50 mm in diameter and 5 mm in width under conditions of the rotation rates of 0-100 rpm. A constant concentration of H$_2$/Ar mixture was supplied into the Y-Li system after the temperature and rotation rate have achieved a steady-state condition. H$_2$ concentration at the outlet of the vessel was determined by a gas chromatograph. H absorption rates in the Y-Li system were compared with numerical calculations. We compared those H absorption rates in the temperature range of 250°C - 400°C under conditions of various rotation rates and activation conditions of Y (Table 1). Before the experiment, a blank test is performed. The results show that the H permeation through vessel wall is negligibly small.

4. Results and Discussion

In this study, a small crucible with small amounts of Li and Y samples is used to shorten the response time. The experimental result on hydrogen absorption rate is compared with previous ones, which use large amounts of sam-

Table 1   Experimental conditions.

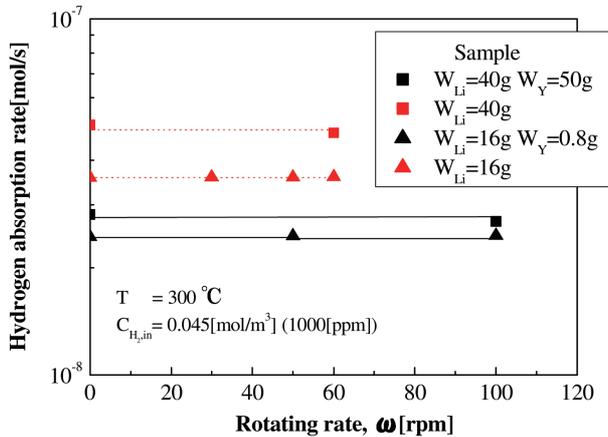| Run No.	Weight of Li [g]	Weight of Y [g]	Temperature [℃]	Flow rate [cm³(NTP)/min]	Rotational rate [rpm]	Inlet H_2 concentration [mol/m³]
1	16	-	250-400	50	0-100	0.045
2	16	0.8	250-400	50	0-100	0.045
3	40	-	300	100	0-100	0.045
4	40	50	300	100	0-100	0.045

Fig. 3   Comparison of the different weight of samples.
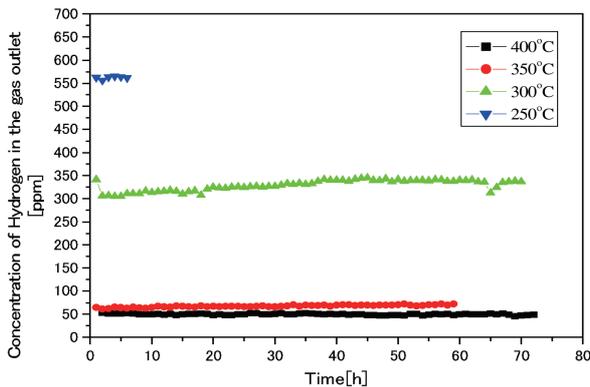
Fig. 4   Time dependence of H_2 concentration in the gas outlet.

Fig. 5   Dependence of mass transfer coefficient on temperature.

ples. Figure 3 shows comparison among hydrogen absorption rates for different weights of the Li and Y samples as a function of rotating rate. Temperature was 573 K and the inlet H_2 gas concentration was 0.045 mol/m³ (1000 ppm). Since the H concentration in Li is low, Li hydride is not formed and H diffuses in liquid Li smoothly. As seen in the figure, the absorption rate does not depend on the rotating rate and the hydrogen absorption rate of the Li + Y system is almost independent of the Li amount. This is because the diffusion in Y is the rate-determining step. On the other hand, when Y is not present in Li, the absorption rate depends on the Li amount. This means that the rate-determining step for the only Li system is H dissociation on Li surfaces.

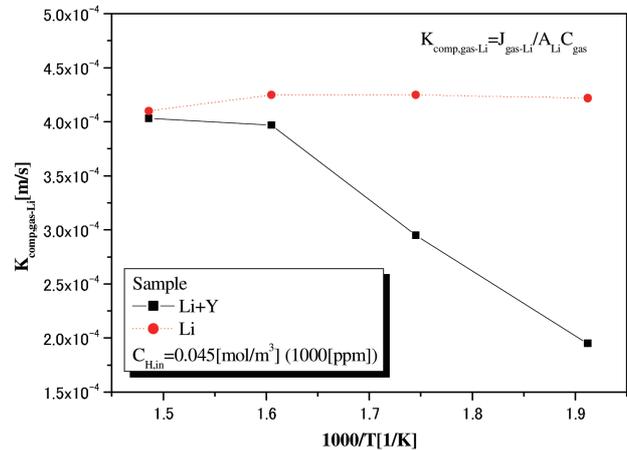Figure 4 shows variations of H_2 concentration in the gas outlet with time when Li and Y are present. The outlet concentration reached a steady-state value immediately after the gas supply. Even time passed over 50 hr, the outlet H_2 concentration for each temperature hardly changed. It has already reached steady state conditions of hydrogen mass transfer in this experiment.

Figure 5 shows the temperature dependence of the mass-transfer coefficient from the gas phase to liquid Li. We determined the mass-transfer coefficient between the gas-phase and liquid Li at range of 523 K - 673 K. Since C_{Li}^* is negligibly small when it is compared to C_{gas}, it is possible to calculate the $k_{comp,gas-Li}$ values by Eq. (1).

As seen in Fig. 5, as the temperature increases, the $k_{comp,gas-Li}$ values for the Li + Y system is increased. On the other hand, the $k_{comp,gas-Li}$ values for the Li system are always higher than that of the Li + Y system and remain constant regardless of temperature. This is because the mass transfer is reduced by the resistance between the gas-phase and the Li + Y system. The $k_{comp,gas-Li}$ value of the Li + Y system shows larger temperature dependence than that of the Li system. So, when temperature is raised high, the value of the Li + Y system becomes closer to that of the Li system.

Figure 6 shows comparison between experimental results and numerical calculation. The experimental result of Run 2 is fitted by a curve calculated by Eqs. (1)-(10). According to the analysis, the $k_{comp,gas-Li}$ value estimated is 2.95×10^{-4} m/s and the k_{Li-Y} value estimated is 1.0×10^{-7} m/s. When H is absorbed in Li without Y, the
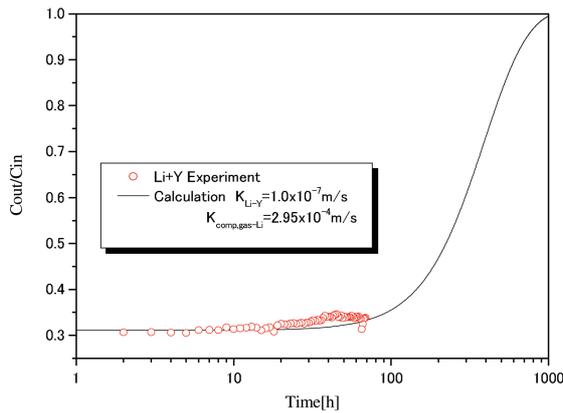
Fig. 6   Comparison between analysis and experiment.

overall process includes (i)-(iv). On the other hand, in the case of the Li-Y system, the two resistances of (v) H migration from Li to Y surface and (vi) diffusion in Y are added to the above four processes. When the process of (i)-(iv) are independent of the presence of Y, the overall mass-transfer rate is delayed by the (v) and (vi) processes.

5. Conclusions

The temperature dependence of the H transfer rate from the gaseous phase to the Li + Y system is investigated in the range of 523-673 K. The rate-determining step for the overall H transfer processes is diffusion through Y. The k_{gas-Li} value of the Li system is always higher value than that of the Li + Y system. The rate-determining step of the Li + Y system is H diffusion through Y. The temperature dependence of the $k_{comp,gas-Li}$ values for the Li + Y system is larger than that of the Li system, where the rate-determining step of the Li system is H dissociation on Li surfaces.

Acknowledgements

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