Study on control of non-metallic impurities in liquid lithium

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Experiments were performed to determine the effective operation condition of Y hot trap, to obtain actual proof based on experimental data under the Li fluidized conditions simulating the International Fusion Material Irradiation Facility (IFMIF), and to verify the performance change of Y hot trap when a trace amount of nitrogen is included in the Li. Controlling impurities in Li is essential for completion of the IFMIF. It is required to demonstrate the performance of the Y hot trap. Impurities limit goals in IFMIF are decided as < 10 wppm for D, and < 1 wppm for T. Before initiating the present study, there was no experimental evidence whether Y can achieve the Li purity goal for hydrogen isotope (D and T) or not. It was proved experimentally that operation of Y hot trap at 573 K is the most stable to recover hydrogen isotopes in Li. The influence of N in Li was investigated to clarify recovery performance of Y hot trap. It was proved Y trap can work effectively even in real IFMIF conditions to achieve the goal of Li purity limit in IFMIF.

Keywords: hydrogen isotopes, liquid lithium, yttrium, mass transport

1. Introduction

In IFMIF, materials irradiation performance will be examined. This examination plays an important role in the engineering design of nuclear fusion reactors. To perform the material irradiation test in IFMIF, high-intensity deuterium beam is applied to flowing liquid Li, to generate high-energy neutrons approximating nuclear fusion reactor condition using the D-Li stripping reactions. At the same time, nonmetallic impurities are included in the liquid Li. Major impurities in Li are hydrogen isotopes (deuterium D, tritium T), and other species (N, C, O). Therefore, control of non-metallic impurities in Li is required from the viewpoints of safety and Li flow stability. Impurities limit goals in IFMIF are determined as < 10 wppm for D and < 1 wppm for T [1].

Yttrium (Y) hot trap is the most effective method to recover the hydrogen isotopes in liquid Li. Y has good compatibility with Li and has higher solubility of hydrogen isotopes than Li. Performance of a Y hot trap was evaluated in the previous study [2], and test results were investigated based on the past experiment to recover H or D under Li static conditions or under Li fluidized conditions. In order to determine the most practical operation temperature of Y hot trap, more experimental data are required.

It is necessary to measure a concentration of hydrogen isotope in Li lower than 10 wppm in IFMIF. We proposed a chemical dissolution method using D-depleted H_2O or HNO_3 in the previous study [3]. There are several other methods by using the hydrogen permeation or electrical conductance, but these methods are not suitable for absolute measurement in IFMIF from the viewpoint of the operation temperature and the required accuracy. In this experiment, the hydrogen isotope concentration in Li or Y was measured using this chemical dissolution method.

In the present study, two experiments on D gettering by Y under Li fluidized conditions were performed. The first one was experiment to realize long-time Li+Y contact and H absorption in a vessel. The second one was experiment to set a Li flow condition simulating the nonmetallic impurities removal system of IFMIF and to evaluate the performance of the Y hot trap. Additionally, a few hundred wppm of N atoms is included into Li inevitably. It is investigated whether or not N pollutes the surface of the Y trap and causes the degradation of the hydrogen recovery performance. However, the experimental data on how much N in Li will influence the performance of Y are insufficient. Therefore, we evaluated how N in Li affects the H recovery performance of Y hot trap.

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2. Experimental

We conducted experiments to realize long-time Li+Y contact and H absorption in a vessel. In this study, we set 3 types of experimental conditions, which are static condition, dynamic one without N and dynamic one with N addition. The samples of Li (purity: 99.9%) and Y (purity: 99.9%) were put in a Mo crucible and heated to 523 K, 573 K or 673 K by an electric furnace. All of Y samples were subjected to HF treatment in order to eliminate oxide on Y surfaces before D absorption. Oxide film on the Y surface was removed by HF treatment, otherwise the film prevents Y from absorbing hydrogen isotopes [4,5]. In the static condition, samples of Li and Y were put in a Mo crucible and a gas mixture with a constant concentration of D_2 in Ar was supplied to the samples to absorb an arbitrary amount of D. In the dynamic condition, we used the experimental apparatus of Fig. 1. A Y plate was put in a bottom of the Mo crucible, and Li was put on the plate. In order to keep sample's surfaces of Li and Y fresh and clean, all the handling was always manipulated in an Ar atmosphere glovebox (Concentration of O_2: lower than 4.0 ppm). Samples of Li were stirred by a SS-316 paddle blade with 50 mm in diameter and 5 mm in width under conditions of the rotation rates of 50 rpm. Initially, a constant concentration of D_2/Ar mixture (approximately 1000 ppm) was supplied to the Li + Y system for 12 hours. We measured the exhaust gas composition by gas chromatograph and converted to the quantity of D absorbed by Li+Y. Then, we changed the gas line from D_2/Ar gas to purge Ar gas (purity: 99.999%), and waited for arbitrary time until a specified diffusion time elapses.
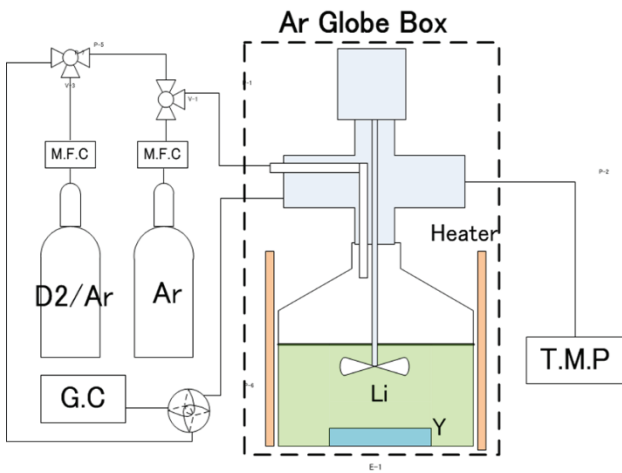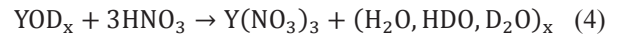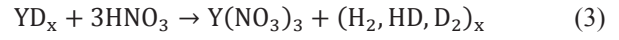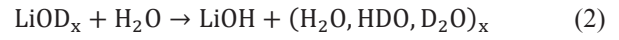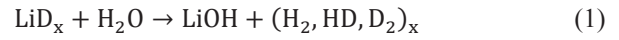

Fig. 1 Schematic diagram of the experiment apparatus for contact of Li with Y under fluidized condition

We used the chemical dissolution method to determine the D concentration dissolved in Y or Li. Fig. 2 shows an apparatus prepared for the chemical analysis. D dissolved in Li or Y was released by the chemical reactions as described below. Hydrogen isotopes absorbed in the sample of Li were released by reaction with D-depleted H_2O. Hydrogen isotopes absorbed in the sample of Y were released by the reaction with HNO_3. These chemical reactions are shown below.

$$LiD_x + H_2O \rightarrow LiOH + (H_2, HD, D_2)_x \tag{1}$$

$$LiOD_x + H_2O \rightarrow LiOH + (H_2O, HDO, D_2O)_x \tag{2}$$

$$YD_x + 3HNO_3 \rightarrow Y(NO_3)_3 + (H_2, HD, D_2)_x \tag{3}$$

$$YOD_x + 3HNO_3 \rightarrow Y(NO_3)_3 + (H_2O, HDO, D_2O)_x \tag{4}$$

The reaction vessel was composed of glass and tubes of SS-316. The apparatus was always purged with Ar gas to prevent samples of Li or Y from contacting with air. The reagent of D-depleted H_2O for Li or HNO_3 for Y was supplied with a syringe set on the samples. The released gases were purged out by Ar gas (purity: 99.999%). The flow rate of Ar gas was 20 cc/min. The concentration of gases emitted from Li and Y were determined by a quadrupole mass spectrometer (QMS). The Mg particle bed was installed just before QMS measurements in order to remove moisture (Q_2O, Q=H, D) in released gas. Q_2O is changed to Q_2 by Mg.
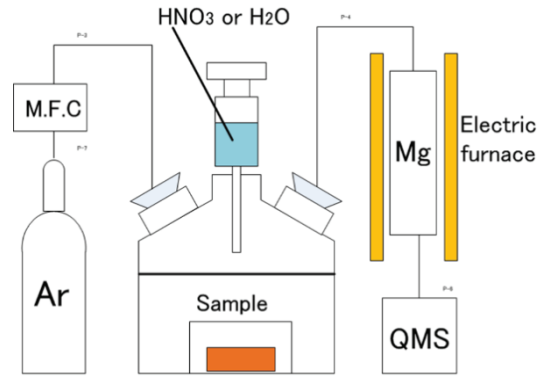

Fig. 2 Schematic diagram of the experiment apparatus for dissolution of Y or Li

Table 1 shows experimental conditions of the samples under static or dynamic Li with or without preliminary N_2 addition. We determined the distribution coefficient of D between Li and Y.

Table 1 Conditions of samples

No	Li condition	T[K]	diffusion time[hr]	amount of samples [mmol]
1	Static (D_2)	573	80	Li:50.5 Y:3.48
2		673	160	Li:59.6 Y:4.28
3	dynamic (D_2)	523	80	Li:72.6 Y:7.84
4		573		Li:23.1 Y:7.42
5		673		Li:119 Y:8.26
6		523	160	Li:28.6 Y:9.56
7		573		Li:93.4 Y:7.62
8		673		Li:115 Y:7.95
9	dynamic ($D_2 + N_2$)	573	80	Li:72.4 Y:7.87

Fig. 3 shows the experimental apparatus for the Li forced-convection flow. The purpose of this experiment is to set a Li flow condition simulating the nonmetallic impurities removal system of IFMIF and to evaluate the performance of the Y hot trap. The Li flow was generated by pressurizing the Li container with Ar gas (purity: 99.999%). At the same time, the entire flow path was held at uniform temperature higher than 453K of melting point of Li (purity: 99.9%). The container was filled up with 1000 g of Li. The height of the Y trap, which made of SS-316 is 260 mm, and the pore size of filter is 15 μm. Y trap was packed with 5.3 g of Y tip. HF treatment is performed to the Y trap in order to eliminate oxide on Y surface before the filling. Initially, a constant concentration of D_2/Ar mixture 1000 ppm was supplied to Li container by bubbling. Then, Li is flown to Y trap by Ar pressurization. Finally, Li sample was taken out from the flow and was analyzed by chemical dissolution method. Table 2 shows experimental conditions of Li forced -convection flow.
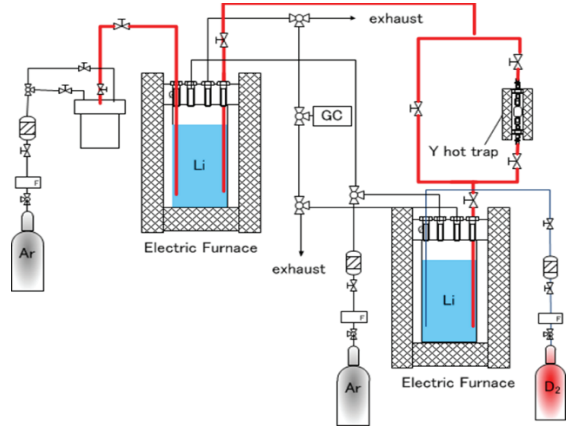

Fig. 3 Schematic diagram of the forced-flow apparatus to investigate the performance of Y trap

Table 2 Experimental conditions

flow rate of Li[cc/min]	T[K]	amount of Li[g]	amount of Y[g]
10	573	1000	5.3

3. Results and discussion

First, results of experiment to realize long-time Li + Y contact and H absorption in a vessel are described. In order to analyze behavior of hydrogen isotope migration from Li to Y, the distribution coefficient was calculated from the experimental result. The distribution coefficient is a ratio between the D concentration in Li and that in Y. It is defined as the bulk D concentration in Li denoted by $C_{D,Li}$ divided by the bulk D concentration in Y denoted by $C_{D,Y}$. The smaller distribution coefficient means more D is transferred from Li to Y. Table 3 shows the result of the

distribution coefficient calculated from the experimental results (No. 1~No. 9). When D recovery from Li to Y approaches to equilibrium, the hydrogen pressures in each sample become equal, so the equilibrium distribution coefficient can be expressed as the ratio of two Sieverts constants. The Sieverts' constants under an equilibrium condition are as follows [6,7]:

$$\frac{c_{D,Li}}{c_{D,Y}} = \frac{K_{D,Li}}{K_{D,Y}} \tag{5}$$

$$K_{D,Li} = 4.74 * 10^{-6} \exp\left(\frac{51372}{RT}\right) \tag{6}$$

$$K_{D,Y} = 2.94 * 10^{-6} \exp\left(\frac{87475}{RT}\right) \tag{7}$$

Fig. 4 shows the equilibrium line and experimental values of the distribution coefficient as a function of temperature. As seen in Fig. 4, D transfer from Li to Y greatly depends on temperature, diffusion time and the conditions of Li. Comparing the data of Li static conditions with those of Li dynamic conditions, it is shown that hydrogen isotope migration to Y is enhanced under Li dynamic conditions than Li static conditions. This is because the diffusion distances of D in the Li dynamic condition is shorter than that in the Li static condition. From a viewpoint of temperature, the recovery performance of Y is most stable when Li temperature is 573 K. The distribution coefficient at 573 K is very close to the equilibrium value.

Table 3 Distribution coefficient of each samples

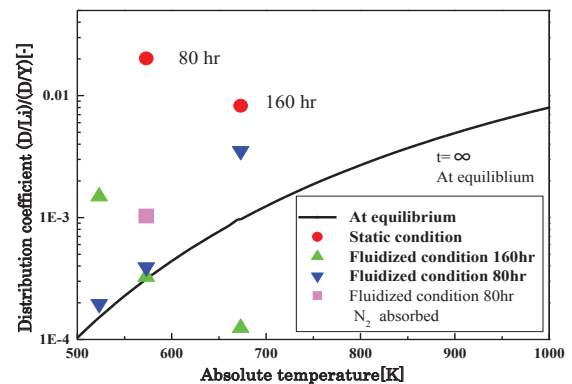| No	Li condition	T[K]	diffusion time[hr]	distribution coefficient $C_{D/Li}/C_{D/Y}$[-]
1	Static (D_2)	573	80	2.02E-02
2		673	160	8.27E-03
3	dynamic (D_2)	523	80	1.96E-04
4		573	80	3.92E-04
5		673		3.52E-03
6		523	160	1.49E-03
7		573	160	3.27E-04
8		673		1.25E-04
9	dynamic ($D_2 + N_2$)	573	80	1.03E-03

Fig. 4 Theoretical and experimental distribution coefficient

Fig. 5 shows the results of N_2 supplying experiments (sample No. 9). The N absorption rate of Li increases gradually. As a result, the total N atom amount in Li reached 430 wppm after supplying Li with N_2 for 2 hours. Since hundreds wppm of N is assumed to be mixed in actual IFMIF Li loop, this N_2 supplying experiment can simulates the IFMIF conditions. On the other hand, as seen in Fig. 4, the value of distribution coefficient for Li sample with N absorption is larger than those without N. This is because N in Li delayed D diffusion and D shift from Li to Y was deteriorated due to Y surface pollution. However, the value of distribution coefficient for Li sample with N absorption is between the static conditions and the dynamic one without N. Therefore, hundreds wppm of N is considered not to degrade the performance of Y greatly.
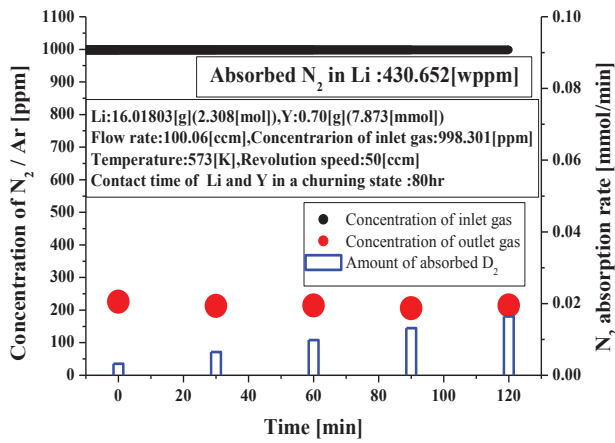

Fig. 5 The nitrogen supply experimental result of sample No. 9

Next, results of experiment for Li forced convection flow are described. Fig. 6 shows an experimental result of D dissolution in Li by D_2 gas bubbling. The D concentration in Li becomes so high that Li is combined with D and forms Li deuteride of LiD. Since the melting point of LiD is 953 K, the fluidization of Li by pressurization is inevitable under this experimental system. Therefore, D was supplied to Li to prevent formation of solid LiD by D_2 gas bubbling. As seen in Fig. 6, all D_2 supplied was absorbed in Li. Li including ppm-level D is formed. The final amount of D in Li was 61.2 wppm. Fig. 7 shows the result of D recovery by Y hot trap under Li forced-convection flow. Table 4 shows the data of this experiment. The more times Li passed Y trap, the more D concentration in Li decreased. Finally the D concentration in Li decreased to the value of 12.7 wppm. We have almost achieved the goal of D recovery in IFMIF.
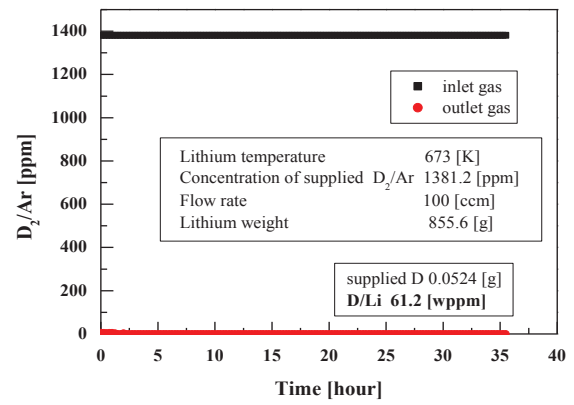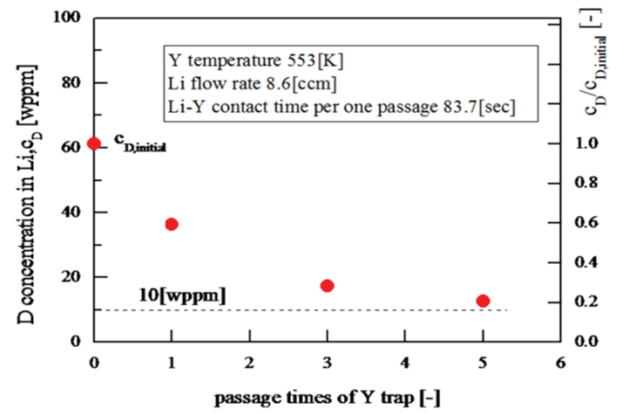

Fig. 6 D dissolution in Li by D_2 gas bubbling

Fig. 7 D recovery under forced convection Li flow

Table 4 Data for recovery rate

passage times of Y trap [-]	Li-Y contact time [sec]	D/Li [wppm]	recovery rate [%]
0	-	61.2	-
1	97.9	36.3	59.4
3	282	17.3	71.7
5	418.4	12.7	79.3

4. Conclusions

We have proved that the most stable operation temperature of Y hot trap is 573 K and demonstrated how the N atoms included into Y through Li affect the D recovery. Under the dynamic condition with 573 K, 80 hr and N of 430 wppm, hydrogen isotope recovery from the Li was not highly influenced by N addition. Based on the experiment of the Li forced-convection flow simulating IFMIF, the D concentration target of IFMIF of <10 wppm have almost been achieved.

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