

Mass loss of Li_2TiO_3 pebbles in atmosphere containing hydrogen

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It has been found that water vapor is released from the ceramic breeder materials into the purge gas due to desorption of adsorbed water and the water formation reaction, and affects the tritium release behavior. Additionally, the release of water vapor possibly promotes the mass loss of Li from the ceramic breeder materials. In this study, we investigated the changes in the mass of Li_2TiO_3 (NFI, CEA) and Li_2TiO_3 with additional Li (JAEA) at elevated temperatures. In hydrogen atmosphere (10,000 ppm H_2/Ar), the Li mass loss is close to be related to the amount of adsorbed water and amount of water formation in each Li_2TiO_3 , and the Li mass loss of Li_2TiO_3 (CEA) is about three times larger than that of the other Li_2TiO_3 pebbles. It is considered that the chemical form of released Li different whether there is the adsorbed water and the water vapor by the water formation reaction in the gas phase or not.

Keywords: ceramic breeders, Li mass loss, surface water, water formation reaction, hydrogen atmosphere

1. Introduction

The present authors have developed an estimation model to represent the tritium release behavior from ceramic breeder materials, which is valid for out-of-pile and in-pile conditions [1, 2]. Tritium release curves estimated by the tritium release model gave good agreements with experimental curves from the ceramic breeder materials under various purge gas conditions [3]. Fig. 1 shows the tritium release model constructed by the present authors. In the model, the tritium diffusion in a breeder grain, tritium transfer to surface water at interfacial layer, and surface reactions on grain surface as adsorption / desorption of physisorbed and chemisorbed water, isotope exchange reaction with hydrogen in purge gas (isotope exchange reaction 1), isotope exchange reaction with water vapor in purge gas (isotope exchange reaction 2), and water formation reaction of hydrogen in purge gas with oxygen in the material are taken into account.

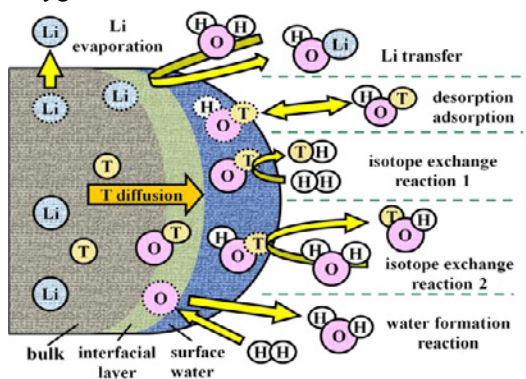


Fig. 1 The tritium release model from ceramic breeder materials

The tritium release behavior from the ceramic breeder materials packed in the blanket module under ITER-like operational condition is estimated based on the tritium release model using parameters obtained in our studies [2]. It is assumed in this estimation that purge gas is He gas mixed with 100Pa H_2 and that physisorbed water is removed completely before operation. The operational condition of ITER is repetition of a burning time of 400 seconds with dwell time of 1400 seconds. This model simplifies the condition of the ITER test blanket module suggested by Japan Atomic Energy Agency (Fig. 2). Fig. 3 shows the tritium release behavior from Li_2TiO_3 (NFI) under the operational condition of ITER. It was estimated that the partial pressure of water vapor in gas phase was about 20Pa and it is kept for about 100hour. This water vapor affects the chemical form of the released tritium. The reaction of released water vapor with the ceramic breeder materials may promote the Li mass transfer. When the ceramic breeder materials are placed at high temperature conditions, a certain amount of Li may evaporate. If non-negligible Li transfer is caused, it would possibly lead to serious issues such as stuffing and erosion of pipes, and drop of TBR. However, the Li mass transfer in a packed bed of the ceramic breeder materials has not been sufficiently understood to date. In the present study, we investigated the changes in the Li mass loss of Li_2TiO_3 (NFI, CEA), and Li_2TiO_3 with additional Li (JAEA) at elevated temperatures in hydrogen atmosphere, and compared them.

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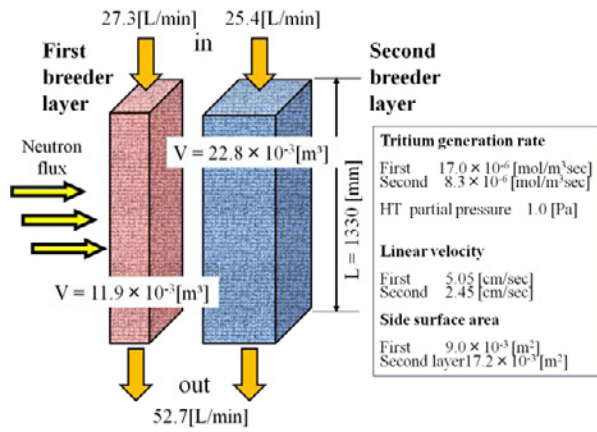


Fig. 2 The ITER-TBM type model

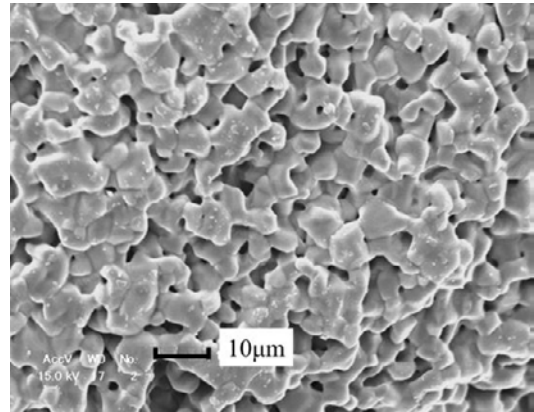


Fig. 4 The SEM picture of as-received Li_2TiO_3 (NFI)

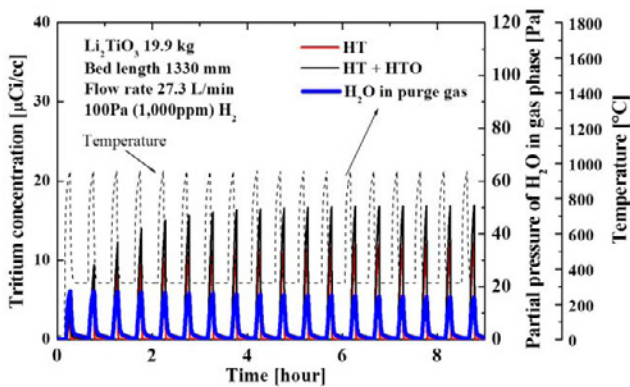


Fig. 3 The simulation result of tritium and water release curve under the operational condition of ITER

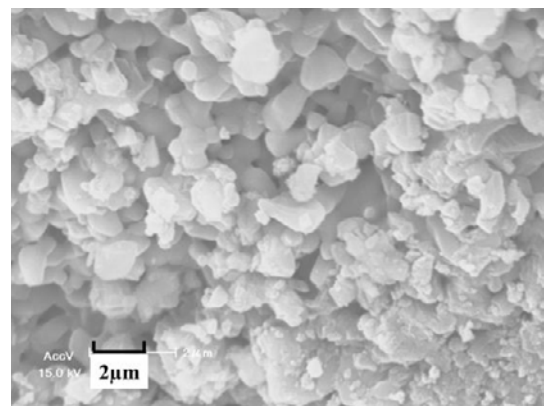


Fig. 5 The SEM picture of as-received Li_2TiO_3 (CEA)

2. Experimental

In this experiment, Li_2TiO_3 pebbles produced by Nuclear Fuel Industry (NFI), Commissariat à l'énergie atomique (CEA), and Li_2TiO_3 with additional Li, 2.06 in Li/Ti ratio, produced by Japan Atomic Energy Agency (JAEA) were used. The Li_2TiO_3 with additional Li is in developmental stage in JAEA as an advanced tritium breeder material for DEMO blanket. The sample pebbles of 0.5 g were packed in a quartz tube, 4 mm in inner diameter, and 36 mm long for Li_2TiO_3 (NFI) and 29 mm for Li_2TiO_3 (CEA), and 29mm for Li_2TiO_3 with additional Li (JAEA) in bed length. Fig. 4, 5 shows a SEM picture of the inside of Li_2TiO_3 (NFI) and Li_2TiO_3 (CEA) pebble. It was estimated from SEM observation that the grain diameter of Li_2TiO_3 is 5 μm for NFI, 1 μm for CEA, and 30 μm for JAEA. Each pebble diameter is 2mm, 1mm, and 1mm, respectively. The details of the experimental procedures were reported in the previous paper [4]. After the desorption of physisorbed water from the sample pebbles by introduction of H_2/Ar (1000Pa H_2/Ar) gas at room temperature, the sample bed was heated to 900 °C, or 600 °C with a ramp rate of 5 °C/min, and the temperature

was held. The water vapor concentration at outlet was measured by a hygrometer (MAH-50, SHIMAZU Co.). The weight changes of sample pebbles were measured before and after the experiment. It is considered that the weight loss of sample pebbles is caused by desorption of adsorbed water vapor, disassociation of oxygen with water formation reaction and release of Li-containing species. In this study, weights of released water vapor and oxygen are subtracted from the weight loss of sample pebbles and the rest is defined as Li mass loss.

3. Result and Discussion

Fig. 6 shows the concentration of water vapor at outlet of the quartz tube when Li_2TiO_3 (NFI) sample bed was heated with a ramping rate of 5 °C/min to 900 °C. It is observed that when H_2/Ar gas is introduced, physisorbed water can be released at room temperature and chemisorbed water is almost removed by elevating temperature to about 400 °C. At over 500 °C, the water vapor is released by the water formation reaction between H_2 and oxygen in the material. The weight of chemisorbed water and oxygen are obtained to be 6.52 $\times 10^{-3}$ g and 1.55 $\times 10^{-3}$ g on average.

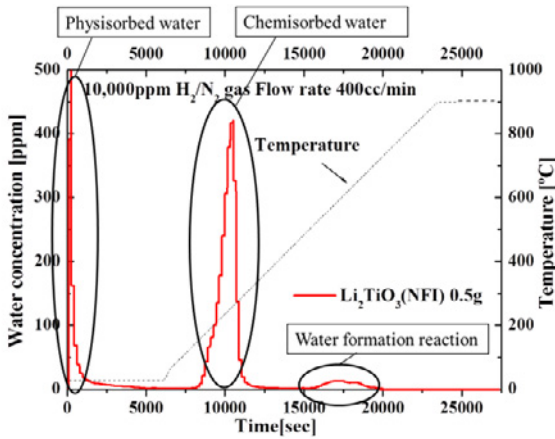


Fig 6 Example of the water release curve from Li_2TiO_3 (NFI)

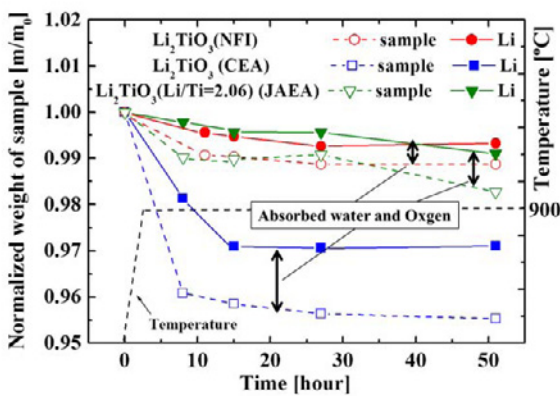


Fig 7 Result of the experiment to the weight changes of sample and mass loss of Li at 900 °C

Fig. 7 shows the weight changes of sample pebbles and the Li mass loss. In the case of Li_2TiO_3 (NFI), the weight loss of sample pebbles is about 1.0 wt% and the Li mass loss is about 0.7wt% after 50hours. The weight of sample seems to be almost steady after 24hours. For the data of Li_2TiO_3 (CEA), a huge mass loss is observed after 8hours. After 50hours, the weight loss of sample pebbles is about 4.0 wt% and the Li mass loss is about 3.0 wt%. In the case of Li_2TiO_3 with additional Li, the weight loss of sample pebbles is 2.0 wt%, and the Li mass loss is about 1.0 wt% after 50hours. It seems that the Li mass loss still continues.

The Li mass loss per gram of Li_2TiO_3 (CEA) is about three times larger than those of Li_2TiO_3 (NFI) and Li_2TiO_3 with additional Li. It is considered that the amount of Li mass loss is related to the difference of surface area and the amount of released water. It is found by the present authors that the amount of chemisorbed water per surface area of Li_2TiO_3 (NFI) are about twice larger than that of Li_2TiO_3 (CEA) and, the amount of generated water per surface area of Li_2TiO_3 (CEA) and that of Li_2TiO_3 (NFI) are almost same. Therefore it is considered that the Li mass loss of Li_2TiO_3 (NFI) is promoted by the release of water vapor,

but we use Li_2TiO_3 (CEA) which surface area is smaller than that of Li_2TiO_3 (NFI) in this experiment, the Li mass loss of Li_2TiO_3 (CEA) is promoted. Fig. 8 shows the relationship between the amount of released water and the Li mass loss. In this figure, the Li mass loss of Li_2TiO_3 (CEA) is three times larger than that of the others, and the amount of released water of Li_2TiO_3 (CEA) is also about three times larger. It is suggested that the Li mass loss is closely associated with the amount of released water from the sample pebbles. The water formation reaction is promoted at high temperatures in hydrogen atmosphere. Therefore it is predicted that the amount of Li mass loss in hydrogen atmosphere is larger than that in dry gas condition, but it is not carried out yet.

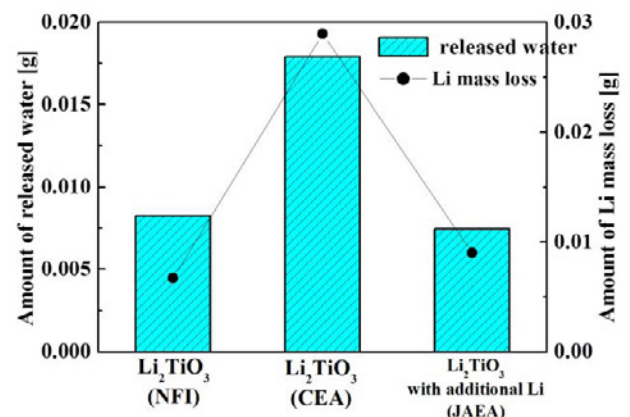


Fig 8 Comparison between the amount of released water and the amount of the Li mass loss

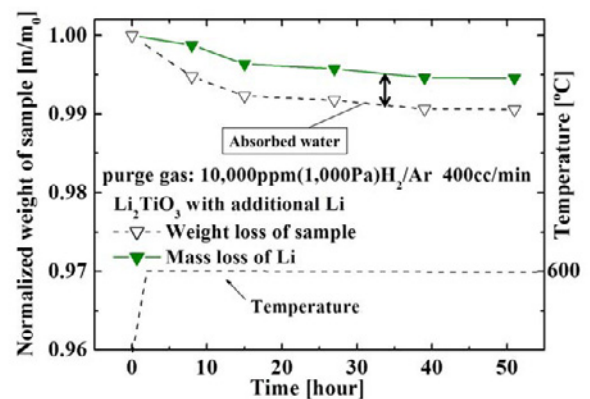


Fig 9 Result of the experiment to the weight changes of sample pebbles and mass loss of Li at 600 °C

Fig. 9 shows the weight changes of sample pebbles when Li_2TiO_3 with additional Li were heated to 600 °C. In this figure, the weight loss of the sample pebbles is 1.0 wt%, and the Li mass loss is 0.5 wt% after 50hours. It is about one-half of the Li mass loss at 900 °C. In the previous studies, it has been found that the amount of generated water by the water formation reaction at 600 °C is smaller

than that at 900 °C for Li_2TiO_3 [5,10]. Therefore it can be said that the Li mass loss at 600 °C is smaller than that at 900 °C because the release of Li by the reaction with generated water at 600 °C is smaller. The weight of sample pebbles seems to be almost steady after 40 hours.

We are also considering that the amount of released water is associated with the method of Li_2TiO_3 manufacturing. By the present authors, Li_2TiO_3 (NFI) is made by the wet process, and Li_2TiO_3 (CEA) is made by the extrusion-spheronization-sintering process. [6, 7] It is considered that the amount of released water is related to whether water is used or not in manufacturing process.

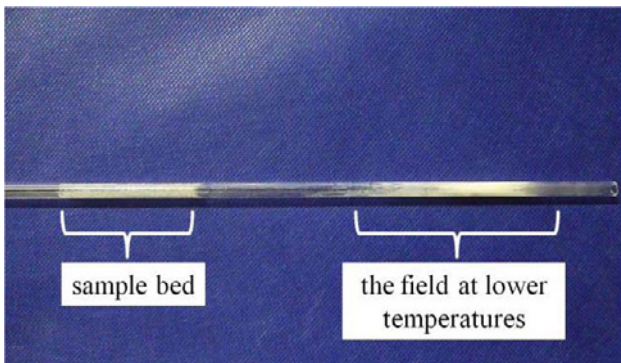


Fig. 10 Picture of the quartz tube after the experiment

Fig. 10 shows the picture of quartz tubes when Li_2TiO_3 (NFI) was used for sample bed after experiment. In this picture, the wall of the quartz tube after experiment is stained with the Li compounds. White turbidity is formed around the sample bed and the downstream region where the temperature is lower than that at the sample bed. It is speculated that Li reacts with the water vapor on the surface of the breeder material and vaporized as LiOH , and then deposits at lower temperature region. White turbidity around the sample bed may be caused by just Li evaporation. It has been observed by Hoshino *et al.* that Li partial pressure is higher than LiOD partial pressure at high temperature under D_2 atmosphere [8]. When the sample bed is held at high temperature for a long time and adsorbed water and the generated water by the water formation reaction expanded completely, and Li would evaporate as Li atoms from the surface of the breeder material slowly.

4. Conclusions

The Li mass loss of Li_2TiO_3 in hydrogen atmosphere is close to be related to the amount of adsorbed water and amount of water formation in each breeder material. The Li mass loss of Li_2TiO_3 (CEA) is about three times larger than that of Li_2TiO_3 (NFI) or Li_2TiO_3 with additional Li (JAEA).

It is obtained that the Li mass loss of Li_2TiO_3 with additional Li (JAEA) at 600 °C is half times larger than that of Li_2TiO_3 with additional Li at 900 °C. It is supposed that the rate of water formation velocity is low at 600 °C, and the amount of released water is less than that of 900 °C.

In hydrogen atmosphere, the chemical form of released Li is different whether there is the adsorbed water and the water vapor by the water formation reaction in the gas phase or not. If there is the adsorbed water and the water vapor by the water formation reaction in the gas phase, the chemical form of released Li is LiOH , and there is no water vapor in the gas phase, Li could evaporate from the surface of Li_2TiO_3 .

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