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Effect of catalytic metals on tritium release from ceramic breeder materials

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Abstract

In most current designs of D–T fusion reactor breeding blankets employing Li-based ceramics as breeder materials, the use of a helium sweep gas containing 0.1% of hydrogen is contemplated to extract tritium via isotopic exchange reactions. However, at temperatures lower than 400 °C, the release process of tritium from the breeders is known to be rather slow. For this reason, there is still a need to develop techniques that promote the release of bred tritium. In order to improve the recovery of tritium from blankets over a wide range of temperature, palladium and nickel were deposited on Li_4SiO_4 pebbles by the incipient wet impregnation method. Out-of-pile tritium release experiments were conducted using the ceramic breeders irradiated in a research reactor. The experimental results reveal the benefit of the addition of catalytic additive metals, which is effective to increase the tritium release rate from ceramic breeder materials especially at comparatively lower temperatures.

1. Introduction

In most current designs of D–T fusion reactor blankets with ceramic breeder materials, tritium bred in breeders such as Li_2O, Li_4SiO_4, $LiAlO_2$, Li_2ZrO_3 and Li_2TiO_3 is extracted using helium sweep gases containing 0.1% of hydrogen. Hydrogen is added to the sweep gases to improve the extraction of tritium via isotopic exchange reactions. However, these exchange reactions taking place predominantly on the grain surface of the ceramic breeders are rather slow at at temperatures lower than 400 °C. Thus, the development of methods to promote the isotope exchange reactions on the grain surfaces are of substantial interest, which could accelerate the recovery of bred tritium particularly at moderate temperatures ranging from 200 to 500 °C of the inherent design.

In previous studies, the isotope exchange reactions and water adsorption at the surface of several ceramic blanket materials were investigated [1–3]. The results indicate that the isotope exchange reaction at the breeder gas/solid interface proceeds fast only at relatively elevated temperatures higher than 700 °C, and thus a considerable decrease in the reaction rate would take place as temperature is decreased. Taking into consideration that there is a broad temperature distribution within a blanket module [2], it is anticipated that the

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tritium bred in regions of lower temperature is poorly recovered, which could result in an increased overall steady state tritium inventory in the blanket module.

In order to accelerate the recovery of tritium from ceramic breeder materials over a broad range of temperatures, the effect of catalytically active metal additives, such as platinum and palladium, on the heterogeneous isotope exchange reactions at the solid breeder/sweep gas interface was examined in a previous work [3]. The results indicate that the isotope exchange reactions on the surface of Li_4SiO_4 are greatly enhanced with such catalytic additives. Evidently, out-of-pile annealing tests with irradiated Pt/Li_4SiO_4 and Pd/Li_4SiO_4 breeders, which contain noble metals in the order of 1 wt%, revealed that the release of tritium from the breeder is accelerated particularly at lower temperatures [4–6]. In this work, the authors investigated the effect of the amount of Pd deposited on the Li_4SiO_4 breeder on the release of tritium from the breeder. Furthermore, the effect of the deposition of Ni on the Li_4SiO_4 on the tritium release was studied.

2. Experimental

Palladium or nickel was deposited on Li_4SiO_4 pebbles (0.51–0.94 mm (av. 0.68 mm) in diameter, >98% TD) by the incipient wet impregnation method generally used for the fabrication of catalysts. Solutions of the palladium tetraammoniumnitrate complex $Pd(NH_3)_4$-$(NO_3)_2$ were used to impregnate the catalytic noble metal in the breeder material. The amount of Pd deposited on the Li_4SiO_4 breeder was controlled by changing the concentration of the complex dissolved in the solutions. For the impregnation of nickel, a solution of the nickel hexaammoniumnitrate complex $Ni(NH_3)_6(NO_3)_2$ was used. Details of the fabrication procedure are cited in our previous reports [3–6]. The breeders fabricated in this way and tested in the out-of-pile annealing experiments were 1.6% Pd/Li_4SiO_4, 0.15% Pd/Li_4SiO_4, 0.015% Pd/Li_4SiO_4 and 2.1% Ni/Li_4SiO_4.

The breeder pebbles were first dried under a dry He stream for 12 h by raising the temperature stepwise up to 400 °C. Then, the breeder pebbles encapsulated in the quartz tubes were irradiated in a thermal neutron reactor (Kyoto University Research Reactor) with a neutron flux of 2.75×10^{13} $cm^{-2}\,s^{-1}$. The irradiation time of the breeders was 2 min. After irradiation, the quartz capsules were mechanically broken, and the breeder materials were removed and placed in a reactor tube made of quartz for the experiments. All these procedures were carried out in a glove box, and thus the breeder materials were never exposed to the atmosphere before and during the experiments.

The temperature of the reactor (containing breeder materials of 0.3 g) was controlled with a conventional electric furnace. A 0.1% H_2/nitrogen gas was used as the purge gas, and the gas flow rate was controlled with conventional mass flow controllers. The gases employed were purified with a trap containing 5 A molecular sieve to remove residual water vapor. The concentrations of tritium in the inlet and outlet streams of the reactor were traced with an ionization chamber. Details of the experiments were cited in previous literature [4–6]. In most cases of the previous work, the reactor temperature was raised stepwise up to 900 °C. However, in this work, the temperature of the reactor was raised at a constant rate up to 900 °C in order to observe the detailed effect of temperature and to avoid temperature fluctuation that takes place when the reactor temperature is raised stepwise. The reactor temperature was kept at ambient temperature before the sweep gas was introduced to the reactor. Even after the sweep gas began to flow into the reactor bed, the temperature of the breeder bed was kept at ambient temperature for several 10 min. Then, the reactor temperature was raised at the rate 5 °C/min up to 900 °C. After the bed temperature reached 900 °C, the reactor temperature was held at 900 °C. Finally, the sweep gas was replaced by a $(0.05\%\ H_2 + 0.5\%\ H_2O)/N_2$ mixture gas to ensure the release of all the tritium bred in the breeders. Introducing a H_2/N_2 gas to a CuO bed of 300 °C generated water vapor.

3. Results and discussion

The solid line in Fig. 1(a) shows the change in tritium concentration in the outlet stream of the reactor as a result of an out-of-pile annealing tests with the virgin Li_4SiO_4 pebbles irradiated in the thermal neutron reactor. The dotted line shows the change in the reactor temperature. The flow rate of the sweep gas (0.1% H_2/N_2) was 100 ml/min. As seen in this figure, the release curve has tow peaks; one peak is observed at 400 °C and the other is observed at 680 °C. The authors repeated the experiment to ensure the reproducibility of the release behavior for the virgin Li_4SiO_4, which lead almost to the same release curve. Abramenkov et al. investigated the tritium release from irradiated Li_4SiO_4 by the out-of-pile annealing method with a 0.1% H_2/He sweep gas and a proportional counter [7]. The heating rate of the breeder in their experiment was 5 °C/min, and thus their experimental procedure is very identical to that of this work. Their result also reveals that there are similar two major peaks in the tritium release curve; one is of the temperature around 400 °C and the other is of around 500 °C. The temperature of the first peak observed in this work is coincident with the result by Abramenkov et al. However, in terms of the second peak, the temperatures where the peaks were observed are different. In this work, the sweep gas was pre-treated with a MS5A adsorption bed to remove residual water vapor before it

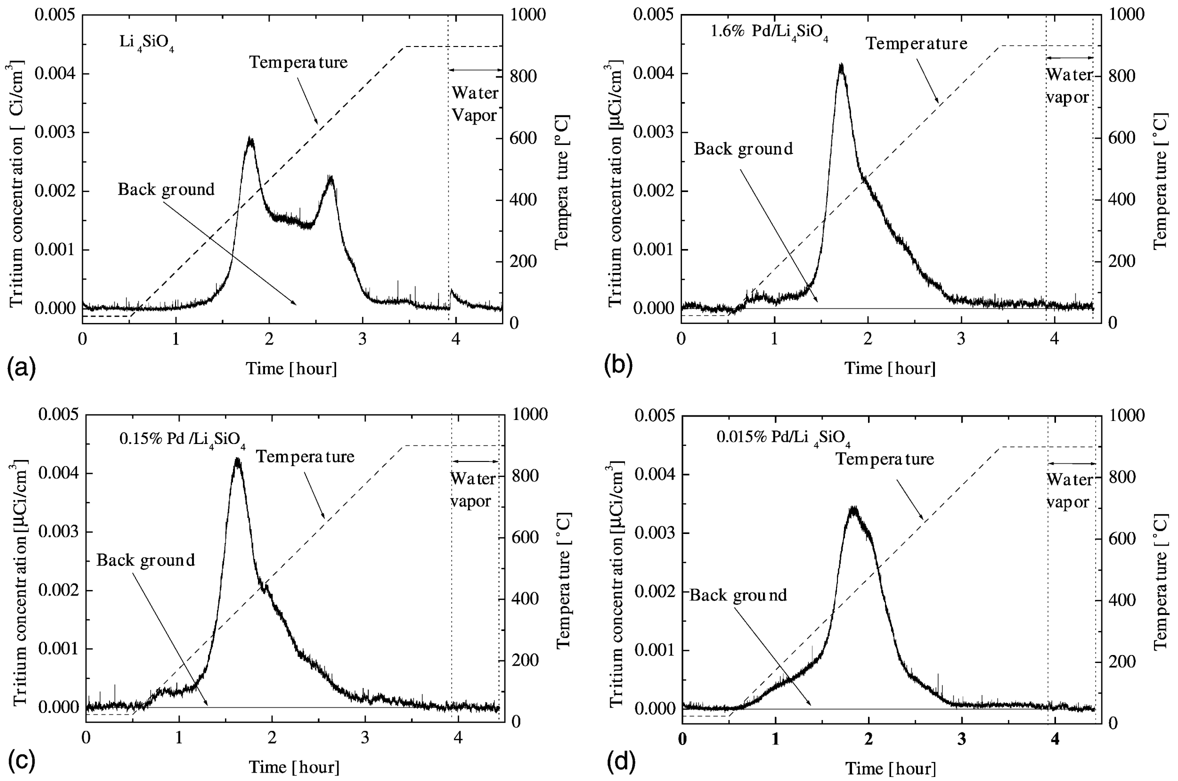

Fig. 1. Out-of-pile annealing test for (a) Li_4SiO_4, (b) 1.6% Pd/Li_4SiO_4, (c) 0.15% Pd/Li_4SiO_4 and (d) 0.015% Pd/Li_4SiO_4 with 0.1% H_2/N_2 sweep gas (amount of breeder: 0.3 g, flow rate: 100 ml/min, irradiation time: 2 min, neutron flux: 2.75×10^{13} cm^2/s).

was introduced to the reactor. But, it is not clear whether Abramenkov et al. conducted such a treatment. One possible explanation for the difference in temperatures of the second release peak could be coexistent water vapor in the sweep gases in the experiments. As far as our experimental results are concerned, the first release peak observed at the lower temperature is considered to be tritium release via grain surfaces with less trapping capability and of diffusion control, whereas the other peak observed at higher temperature could be tritium release from grain surfaces with greater trapping capability. Although the tritium level has nearly the same background level at 900 °C, tritium was again released when the sweep gas was replaced with that containing water vapor. In total, 30.3 μCi of tritium was released. 98.4% of the total tritium was released with the 0.1% H_2/N_2 sweep gas and the remaining amount of tritium (1.6%) was released with the H_2+H_2O/N_2 sweep gas.

The results of out-of-pile annealing tests for the 1.6% Pd/Li_4SiO_4 breeder are shown in Fig. 1(b). In total, 31.5 μCi of tritium was released. Just after the bed temperature was raised from room temperature, an increase in tritium concentration in the outlet stream of the reactor was observed, which was not observed in the case of the virgin Li_4SiO_4 breeder. Only one peak was observed in the tritium release curve, which is a great difference compared with the release curve for the virgin Li_4SiO_4. The peak tritium release was observed at the temperature slightly lower than 400 °C, and the peak release temperature is almost coincident with the first peak release temperature observed for the virgin Li_4SiO_4. The peak tritium concentration in the release curve is apparently higher than that observed in the case of virgin Li_4SiO_4. No tritium release was observed when the sweep gas was changed to the N_2 gas containing 0.05% of H_2 and 0.5% of H_2O at 900 °C. This is probably because all the bred tritium is released at lower temperatures with the help of Pd that enhances the surface exchange reaction. These results are similar to the results obtained in our previous study [4–6], indicating that the addition of Pd in the order of 1% to the Li_4SiO_4 breeder is an effective way to enhance the tritium release rate at low temperatures.

The result of out of pile annealing test for the 0.15% Pd/Li_4SiO_4 breeder is shown in Fig. 1(c). 34.5 μCi of tritium was totally released. As observed in the case of the 1.6% Pd/Li_4SiO_4 breeder, an increase in tritium concentration in the outlet stream of the reactor was also observed just after the bed temperature was raised from ambient temperature. Only one peak was observed in the tritium release curve as was observed for the 1.6% Pd/Li_4SiO_4 breeder. The tritium release curve obtained is almost coincident with that obtained for the 1.6% Pd/Li_4SiO_4 breeder, and thus it can be said that deposition of as small as 0.15% of Pd gives almost the same effect for the enhancement of tritium release.

Fig. 1(d) shows the result of out-of-pile annealing tests for the 0.015% Pd/Li_4SiO_4 breeder. 31.2 μCi of tritium was totally released. As observed in the case of the 1.6% and 0.15% Pd/Li_4SiO_4 breeders, an increase in tritium concentration in the outlet stream of the reactor was also observed just after the bed temperature was raised from ambient temperature. Only one peak was also observed in the tritium release curve, and the peak tritium release was also observed at 400 °C. The tritium release curve obtained is somewhat different from that obtained for the 1.6% and 0.15% Pd/Li_4SiO_4 breeders; the tritium release curve is broadened to some extent compared with the results for the 1.6% and 0.15% Pd/Li_4SiO_4 breeders. However, it can be said that deposition of as small as 0.015% of Pd is still effective for the enhancement of tritium release. The results shown above suggest that the amount of Pd deposited on Li_4SiO_4 can be considerably decreased and deposition of Pd in the order of as large as 1% is not necessary. This means that the problem of cost related to the use of noble metals is less significant.

Fig. 2 shows the change in tritium concentration in the outlet stream of the reactor as a result of an out-of-pile annealing tests with the 2.1% Ni/Li_4SiO_4 breeder. As seen in this Fig. 2, the release curve has two peaks; one peak is observed at 400 °C and the other is observed at 470 °C. The second release peak is observed at a slightly higher temperature than that of the first peak release temperature. A small amount of tritium was released when the sweep gas was replaced with that containing

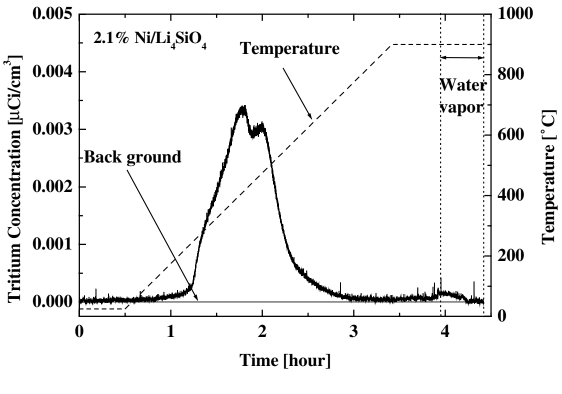

Fig. 2. Out-of-pile annealing test for 2.1% Ni/Li_4SiO_4 with 0.1% H_2/N_2 sweep gas (amount of breeder: 0.3 g, flow rate: 100 ml/min, irradiation time: 2 min, neutron flux: 2.75×10^{13} cm^2/s).

water vapor. 32.4 μCi of tritium was totally released. The presence of two peaks in the release curve and tritium release with the sweep gas containing water vapor could indicate that the catalytic effect of Ni is smaller than that of Pd. However, in comparison with the result for the virgin Li_4SiO_4 breeder, bred tritium is released at apparently lower temperatures, and thus the deposition of Ni on the Li_4SiO_4 breeder is also effective for the enhancement of tritium release rate at lower temperature. This result suggests that not only noble metals but also base metals can be used for the catalyst to enhance the tritium release at lower temperatures. In terms of Ni, the deposition of higher concentrations appears to be necessary to obtain the promotion effect that is comparable to Pd.

In the experiments shown above, tritiated species released from the irradiated breeder materials were not distinguishable, since the total tritium level was in the process gas was only traced with one ionization chamber. Thus, the authors are now in the process of preparing a new monitoring system with two ionization chambers and a water bubbler to obtain more detailed information on the tritiated species released from the breeders.

4. Conclusions

Catalytic breeder materials were produced by impregnating a Li_4SiO_4 breeder with either Pd or Ni. Out-of-pile annealing experiments were conducted using irradiated ceramic breeders. The results of the experiments indicate that tritium bred in the catalytic breeder material is released at lower temperatures compared with the breeder material with no catalyst. It was found that the deposition of a substantially smaller concentration of Pd as low as 0.015% is still effective to promote the tritium release. It was also experimentally confirmed that the deposition of Ni on the Li_4SiO_4 breeder is also effective for the enhancement of tritium releases rate at lower temperatures.

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