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Exchange of tritium implanted into oxide ceramics for protium by exposure to air vapors at room temperature

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Abstract

The exchange of tritium, implanted into an oxide ceramic with a pure tritium ion beam, for protium by exposure to normal air at room temperature has been measured in a collaboration experiment with the Tritium Laboratory group, JAERI. It is shown that the release of THO produced by the exchange $H_2O + T \rightarrow THO + H$ at the surface of the crystallites decreases monotonically with exposure time, while the release of TH gas increases in the beginning, reaches a maximum and decreases monotonically as the time increases. The latter behavior of TH gas release gives an important evidence for bulk recombination of H uptaken from the surface with T implanted. These results are discussed based on the one-way diffusion model proposed previously for the explanation of the D–H exchange experiment.

1. Introduction

The dynamic behavior of hydrogen isotopes in the bulk and at the surface of oxide ceramics has received intensive attention from applied point of views such as high temperature protonic conductors in electrochemical devices and tritium breeding materials in fusion devices. Up to now, many efforts have been performed by many authors [1], for understanding the dynamic behavior of hydrogen isotopes in proton-conductive ceramics, with use of various experimental techniques such as conductivity measurement [2], luminescence spectroscopy [3], neutron scattering and diffraction [4], and nuclear reaction analysis with high energy ion beams [5]. The present author group has also studied the thermal behavior of H and D implants in $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ by means of the elastic recoil detection measurement with an MeV He^+ ion beam [6]. This technique is very powerful to investigate isotope effects in dynamic behavior of H and D in materials [7].

Very recently, it has been found eventually by the present author group that D implants in $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ are almost completely exchanged for H by exposure to normal air introduced into the vacuum chamber at room temperature [8]. Similar exchange of D–H has been observed for single crystalline $SrTiO_3$ implanted up to the saturation concentration [9]. It has been found, however, in the vice versa case that H implants in the ceramic are hardly exchanged for D in D_2O vapor carried into the vacuum chamber by dry-air passing through a D_2O water container. It has been quantitatively determined from the experimental data on the exchange curves as a function of exposure time that

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the ratio of the D–H exchange rate to the H–D exchange rate in the beginning is roughly 100 at room temperature [10,11], which is an anomalously large isotope difference in the hydrogen isotope exchange rate in the oxide ceramic.

The above experimental observation of the anomalously large isotope effect has not been reasonably explained in terms of the conventional round diffusion model, but of a one-way diffusion model [11]: adsorption of OH^- and absorption of H^+ due to the dissociation of H_2O at the surface, diffusion of H^+, and release of D implants from a trapping site due to bulk recombination with uptaken H^+ and the subsequent occupation in the vacant trapping site by uptaken H^+. According to the one-way diffusion model, the anomalously large isotope difference is attributed to a dissociative adsorption rate of the water molecule at the surface and diffusion of hydrogen in the bulk and it is also noted that D trapped in the bulk is released as a mixed molecule gas of HD.

For tritium breeding ceramic materials, important issues concerning the hydrogen dynamic behavior are recovery of tritium produced during reactor operation, reduction of tritium inventory and removal of tritium from the burnt breeding materials for maintenance. Current systems for tritium recovery from the blanket are based on the aspect that the release of T from the breeding materials takes place due to the molecular recombination at the surface following thermally activated diffusion from the bulk. Improvement or enchancement of the tritium recovery due to isotope exchange at the surface of T and purge gas of H_2 of H_2O added to the He sweep gas has been experimentally proven by in-pile and out-of-pile experiments [12]. The model of one-way diffusion from the surface into the bulk proposed for explanation of the experimental result by the present author group suggests that the use of H_2O for purge gas brings about the improvement more efficiently than only the exchange of $H_2O + T \rightarrow THO + H$ at the surface, because the exchange product of H releases T due to the bulk recombination and the exposure of the D-implanted specimen to H_2 gas hardly induce the D–H exchange [9]. Moreover, it has been observed that the similar D–H exchange at room temperature takes place in Li-containing oxide ceramics such as Li_2ZrO_3 and Li_2TiO_3 [13,14], considered as tritium breeding ceramics, although the D–H exchange speeds in them are by an order of magnitude slower, than in $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$. For establishment of the validity of the one-way diffusion model and practical applications, further detailed understanding of the hydrogen isotope exchange processes is of essential importance.

In this paper we report the experimental results on the exchange of T, implanted into $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ with 1 keV ion beam of pure tritium, for H by exposure to normal air at room temperature which has been tested from measurements of the contents of HTO and HT in the normal air flowing through the sample container, because of its high exchange speed. It is shown that the content of THO produced by the exchange of $H_2O + T^+ \rightarrow THO + H^+$ at the surface of the crystallites decreases monotonically with exposure time, while the content of TH increases in the beginning, reaches a maximum and then decreases monotonically as the time increases. These results are discussed with the post-thermal desorption experiment based on the one way diffusion model described above.

2. Experiments

The specimen used was a disc of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ of 15 mm in diameter and of 2 mm in thickness (crystallite size: $\simeq 1$ μm in diameter), which was prepared by solid state reaction and sintering process [15]. The specimen was mounted on the sample holder in the tritium permeation apparatus (TPA) of the Tritium Laboratory in JAERI, which is composed of a Duo Pi Gatron ion source, the main chamber, a tritium supply and recovery system and a tritium detection system. The details of TPA were described elsewhere [16]. The specimen was implanted with 1 keV pure tritium ion beam of 8 mm in diameter at a flux of 8.3×10^{14} T^+/cm^2 s for 5 h at room temperature. The total T^+ fluence was estimated to be 5×10^{18} T atoms/cm^2 at the target surface. The projected range of 1 keV T_2^+ ions in the specimen was estimated to be around 10 nm and the saturation concentration to be $5 \times 10^{21}/cm^3$ from the experimental data on the 5 keV D_2^+ ion implantation [8].

The T-implanted specimen was transferred to the sample container, in which the specimen was exposed to normal air or nitrogen gas flowing into a two-stage tritium collector: the first stage is a THO bubbling collector and the second stage a TH collector. The contents of THO and TH released by exposure of the specimen to normal air and nitrogen gas were measured with the system as a function of the exposure time for 24 h at a flow rate of 50 cm^3/min at 292 K.

After the exposure experiment, the thermal desorption was performed with each specimen, which was heated up to 1273 K at a temperature rise speed of 0.5 K/s by an infrared irradiation heating system. The six kinds of gas species with the mass-to-electronic charge ratios of $M/e = 4$ (HT), 5 (DT), 6 (T_2), 18 (H_2O), 20 (HTO) and 22 (T_2O) were measured as a function of heating time at each 4 s by means of a quadrapole mass spectrometer.

Finally, total contents of tritium retained in the specimen after the thermal desorption experiment were measured for two months. The result will be described elsewhere.

3. Experimental results and discussion

The contents of T released from the T-implanted specimens exposured to normal air and nitrogen gas flowing obtained as a function of the exposure time are shown in Table 1, where the contents of T in the chemical states of HTO and TH are expressed in units of Bq in each exposure. In both exposures, it is seen that tritium is mainly released as the chemical state of HTO and the content of T decreases rapidly within 3 h and hereafter gradually. On the other hand, it is clearly seen that the content of T in the chemical state of TH is by an order of magnitude lower than in the chemical state of THO and the content of TH increases in the beginning, reaches a maximum at 3–6 h and then decreases monotonically. The release of HTO and TH on the nitrogen gas exposure by a factor of 4 lower than on the air exposure is ascribed to the adsorption of H_2O vapor during transfer of the T-implanted specimen from the main chamber of TPA to the sample container for the gas exposure experiment. The reason for the limited release of tritium is attributed to smallness in the adsorption of H_2O vapor during the transfer process.

The experimental result that the main component released on the normal air exposure is THO suggests that the direct exchange of T retained for H in H_2O vapor takes place at the surface and in the grain boundaries of the specimen. The maximum release of TH at the exposure time of 3–6 h also suggests that H uptaken through dissociative adsorption of H_2O or direct exchange of T for H in H_2O at the surface and in the grain boundaries induce release of T as TH molecule from the bulk. The latter result has been obtained, for the first time, in this experiment. Moreover, it gives an evidence for the one-way diffusion model proposed from the D–H exchange experiment. The large difference between the contents of THO and TH is ascribed to the large ratio of retained numbers of T at the surface and in the grain boundaries to those in the bulk which is responsible for the low implantation energy.

Here, the results on the thermal desorption experiment performed after the exposure experiment are

Table 1
The contents of HTO and HT released from the T-implanted specimen of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$, by exposure to normal air and nitrogen gas flowing at a flow rate of 50 cm^3/min and at 292–293 K measured as a function of the exposure time

Time	Chemical form			
	Air flow		Nitrogen gas flow	
	HTO (Bq)	HT (Bq)	HTO (Bq)	HT (Bq)
0–3 h	4.30×10^7	1.29×10^6	1.09×10^7	1.92×10^5
3–6 h	8.10×10^6	3.60×10^6	1.84×10^6	3.96×10^5
6–12 h	5.26×10^6	9.14×10^5	1.89×10^6	4.79×10^4
12–24 h	7.81×10^6	2.56×10^5	2.84×10^6	7.19×10^4
Sub total	6.42×10^7	6.06×10^6	1.75×10^7	7.08×10^5
Total	7.03×10^7		1.82×10^7	

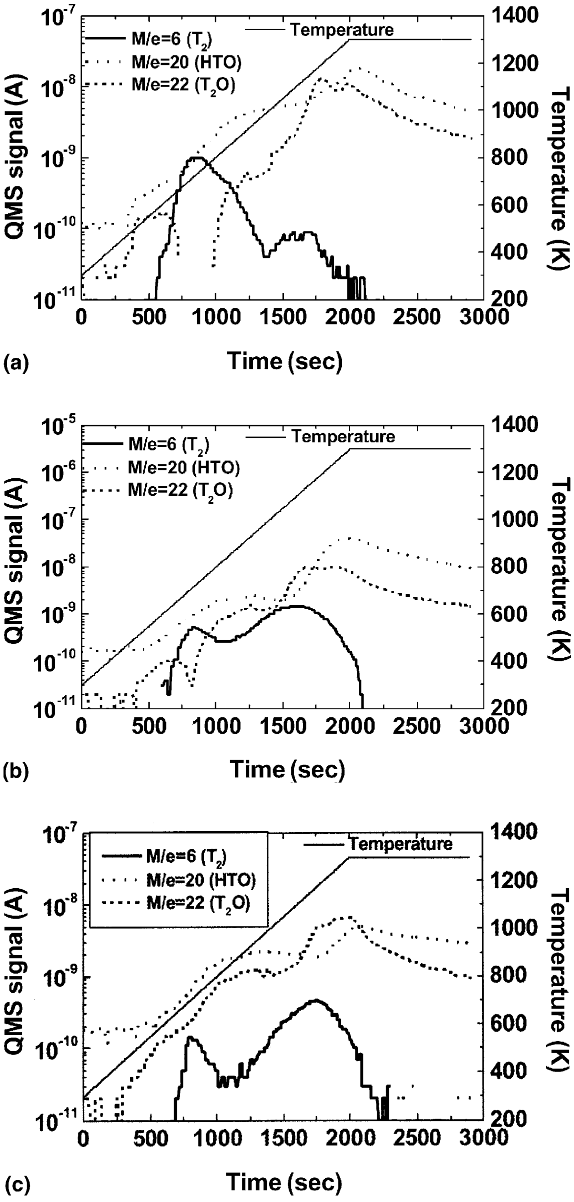

Fig. 1. The thermal desorption spectra of three kinds of species with the mass number to electronic charge ratios $M/e = 6$ (T_2), 20 (HTO) and 22 (T_2O) released form the T-implanted specimen of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ only transferred to the sample container (a), transferred to the sample container and exposed to normal air (b) and transferred to the sample container and exposed to nitrogen gas (c) which were heated up to 1273 K at a temperature rise speed of 0.5 K/s by the infrared irradiation heating system.

described. The thermal desorption spectra obtained for the specimens, only transferred to the sample container (a), transferred to the sample container and exposed to normal air (b) and transferred to the sample container and exposed to nitrogen gas (c) are shown in Fig. 1(a)–(c), respectively, where the signals of the mass number 6 (T_2), 20 (HTO) and 22 (T_2O) are plotted. The signal of the mass number 5 (DT) was found to be very small compared with the other species, which indicates that the background level of D atoms in the specimen is very low, thus we do not need to consider the reaction of $D + T$. It is seen from Fig. 1 that the release of the mass number 6 takes place in two stages, the mass number 20 also in two stages and the mass number 22 in three stages.

According to the experimental data obtained by means of the ion beam analysis, the lowest temperature stage takes place due to release from the bulk and the other stages from the grain boundaries. Thus, the largest release of the mass number 6 from the specimen (a) without any exposure corresponds well to the result on the exposure experiment. The larger release of the mass number 20 (THO) at the low temperature stage takes place for the specimens (a) and (c) without direct exposure to air. The result indicates that the content of HTO has been released from the specimen (b) on the exposure to air and the number of T retained has been reduced, which is also reasonable.

The mass number of 22 (T_2O) is considered to be produced by the cascade exchange activated thermally at the surface and in the grain boundaries due to the reactions of $H_2O + T \rightarrow THO + H$ and $THO + T \rightarrow T_2O + H$. In such a case, the release of T_2O from the specimen (6) is expected to be the lowest because the retained number of T is the lowest, which is consistent with the experimental observation (Fig. 1(b)).

It is clearly seen from Fig. 1 that the release of all species at the higher temperature stage is much larger than at the lower temperature stage. The result indicates that the tritium content retained in the bulk by the low energy implantation is much lower than in the grain boundaries, which is ascribed mainly to the large diffusion constant of tritium in the grain boundaries and partly to too low energy of the implanted tritium ion beam. Such a result has been observed, for the first time, in the experiments of the pure tritium implantation and subsequent thermal desorption. The fact result is very useful for estimation of the tritium inventory in the polycrystalline materials exposed to energetic tritium ions.

4. Summary

The exchange of tritium, implanted into a ceramic of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ with 1 keV pure tritium ion beam, for protium by exposure to normal air at room temperature and the thermal desorption spectra of six species with the mass number to electronic charge ratios of 4, 5, 6, 18, 20 and 22 released from the specimen after exposure to air have been measured in a collaboration experiment with Tritium Laboratory group in JAERI.

It has been found in the air exposure experiment at room temperature that the release of THO produced at the surface of the crystallites in the specimen decreases rapidly and monotonically, which the release of TH gas increases in the beginning, reaches a maximum and decreases monotonically as the exposure time increases. The former result indicates that the H_2O molecule is directly transferred into HTO by the reactions $H_2O + T \rightarrow THO + H$ or $OH^- + T + H^+ \rightarrow THO + H^+$ at the crystallite surface in the very beginning of T–H exchange at room temperature. The latter result gives an important evidence for bulk recombination of T–H in the crystallites, involved in the one-way diffusion model for D–H exchange.

It has been also found in the thermal desorption experiment that the release of all species from the specimen takes place in two stages or three stages and the release contents from the bulk at the lower temperature are much smaller than those from the grain boundaries at the higher temperature.

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