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Tritium release from Li_2O studied by infrared absorption spectroscopy

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Abstract

Desorption of a surface hydroxyl group of –OD on Li_2O into the sweep gas of dry Ar, Ar + H_2 or Ar + H_2O was studied by using a diffuse reflectance method with Fourier transform infrared absorption spectroscopy under controlled H_2O (D_2O) or H_2 (D_2) partial pressure. Under a D_2O containing atmosphere, multiple peaks due to surface –ODs were observed in the O–D stretching vibration region and they showed different dependencies on temperature or D_2O vapor pressure. The surface –OD observed at 2660 and 2520 cm^{-1} was removed by drying under Ar gas at 833 K. However, surface –OD at 2900, 2540 and 2490 cm^{-1} stayed on the Li_2O surface up to 973 K. In order to remove these –ODs at 833 K, addition of H_2 to the sweep gas was needed. It was also found that desorption of surface –OD was affected by the oxygen partial pressure near the surface. We also compared the observed results with those of in situ tritium release experiments (TTTEx). © 1997 Elsevier Science B.V.

1. Introduction

In order to design the fusion reactor fuel cycle, a thorough understanding of tritium release behavior from the ceramic breeder material is required. From in-pile and out-of-pile tritium release experiments and modeling studies, it has been pointed out that surface desorption is often the rate-determining process of tritium release [1,2].

On the surface of lithium oxide, which is a candidate for the solid breeding material, tritium is considered to exist as a hydroxyl group of –OT. The vibration frequency of O–T bonding is affected by the bonding nature of –OT to the surface. Therefore, it is possible to study the nature of the hydroxyl group on the surface by the observation of O–T stretching vibrations. In the authors' previous works [3,5], it was found that the Li_2O surface is not homogeneous for D_2O adsorption and the nature of the hydroxyl group is affected by the chemical composition of the sweep gas.

In the present paper, we focused on the desorption of a surface hydroxyl group of –OD into the sweep gas of Ar, Ar + H_2 and H_2O by observing the stretching vibration of the surface –OD. We also tried to compare the results with in situ tritium release experiments (TTTEx [4]).

2. Observation of surface hydroxyl group by FT-IR

2.1. Experimental

Infrared absorption spectra were recorded using a Shimadzu FT-IR 8100 with a resolution of 2 cm^{-1}. In order to observe the absorption spectra of powdered samples, the diffuse reflectance method was used. The sample of Li_2O used in this work was supplied from Furuuchi (purity 99.9%). Before use, the sample was heated up to 1073 K under vacuum to desorb H_2O or carbonate in Li_2O. Then it was sieved into powder (about 45 μm) and was placed in the sample holder. The temperature of the sample could be controlled from room temperature to 973 K by the heater attached under the sample holder. The atmosphere in the chamber was controlled by the sweep gas of dry Ar, Ar + D_2O, H_2O (1–400 Pa) or Ar + D_2, H_2 (0–1000 Pa). When D_2 containing gas was introduced into the system, the generation of water was confirmed. This is considered to be owing to the reaction at high temperature between D_2

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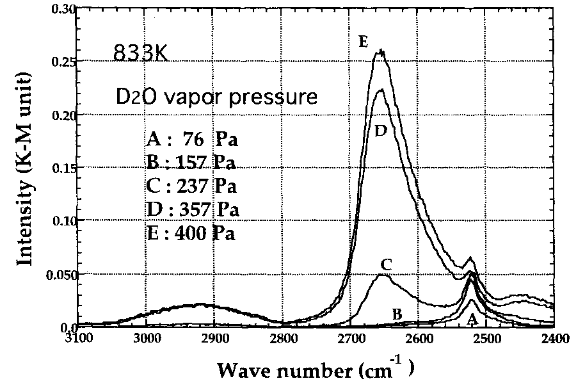

Fig. 1. Absorption spectra of Li_2O under D_2O vapor at 833 K.

Table 1
Assignment of observed peaks to the surface nature [6]

Observed peaks	Surface nature
2900 cm^{-1}	Many O^{2-} exist around the –OD, on modified surface by heat treatment at 973 K
2748 cm^{-1} 2717 cm^{-1}	'Isolated' deutroxyl groups with several adjacent O^{2-}
2660 cm^{-1}	–OD with several adjacent –OD
2540 cm^{-1} 2490 cm^{-1}	–ODs with small number of O^{2-} in the neighbor
2520 cm^{-1}	Adsorbed on the most active site

and the oxide layers on apparatus components or Li_2O sample and D_2. Therefore, the atmosphere near the sample is composed of Ar, D_2O and D_2 when D_2 is added to the sweep gas.

2.2. *Observation of surface –OD under D_2O or D_2 atmosphere*

In previous work, we observed plural absorption peaks attributed to hydroxyl groups of –OD on the Li_2O surface. These peaks showed different dependence on temperature and partial pressures of D_2O or D_2 in the atmosphere [5–7]. Figs. 1 and 2 show the typical absorption spectra of Li_2O under D_2O or D_2 atmosphere, respectively [6]. Several absorption peaks attributed to surface hydroxyl groups were observed in the O–D stretching vibration region. Under a low D_2O vapor pressure, only the peak at 2520 cm^{-1} was observed. This peak became larger with increasing D_2O vapor pressure up to 157 Pa and a peak intensity at 2520 cm^{-1} was saturated above 157 Pa. The peak at 2660 cm^{-1} appeared only under higher D_2O vapor pressure.

Under a D_2 containing atmosphere, we can observe a remarkable difference compared with D_2O added sweep gas. First, the intensity of the peak at 2660 cm^{-1} was reduced compared with that of Ar + D_2O sweep gas. In particular, the peak at 2660 cm^{-1} was not observed at 833 K although an appreciable amount of D_2O vapor exists under this condition. Second, a broad band was observed around 2700–2400 cm^{-1}. This band is considered to be from the overlap of three peaks, 2540, 2520 and 2490 cm^{-1}. It is considered that the increase of the peaks at 2540 and 2490 cm^{-1} caused the broadness of this band.

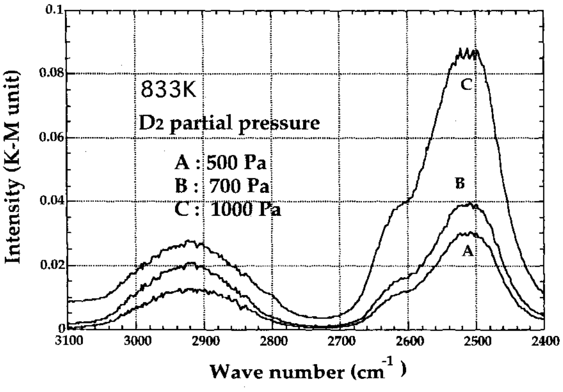

Fig. 2. Absorption spectra of Li_2O under D_2 at 833 K.

O–D stretching vibration of surface –OD can be affected by the chemical species (O^{2-}, Li^+, oxygen vacancy, OD^-) around the noticed –OD. Table 1 shows our assignment of the observed peaks which was determined from experimental results [7].

2.3. *Desorption of surface –OD into the sweep gas*

In order to observe the desorption of surface –OD into the atmosphere, we performed the following experiments. First, D_2O or D_2 was added to the sweep gas and –OD was produced on the sample surface. Then the sweep gas was changed to dry Ar, Ar + H_2 (3400 Pa) or Ar + H_2O (320 Pa) in order to desorb –OD into the sweep gas. We observed the change of absorption spectra in the O–D stretching vibration region during desorption.

Fig. 3 shows the change of absorption spectra when the sweep gas was changed from D_2O (320 Pa) to dry Ar gas at 833 K. Under a D_2O atmosphere, several peaks were observed in the O–D stretching vibration region. According to previous studies [6], they were deconvoluted into five peaks at 2900, 2660, 2540, 2520 and 2490 cm^{-1}. Among these peaks, those at 2660 and 2520 cm^{-1} decreased under dry Ar atmosphere, and after 8 h they completely vanished. This observation means that surface –OD adsorbed on this site could be removed by drying at 833 K. However, hydroxyl groups adsorbed on the sites corresponding to peaks at 2900, 2540, and 2490 cm^{-1} could not be desorbed under Ar atmosphere at 833 K in 12 h and we observed a change in absorption spectra at

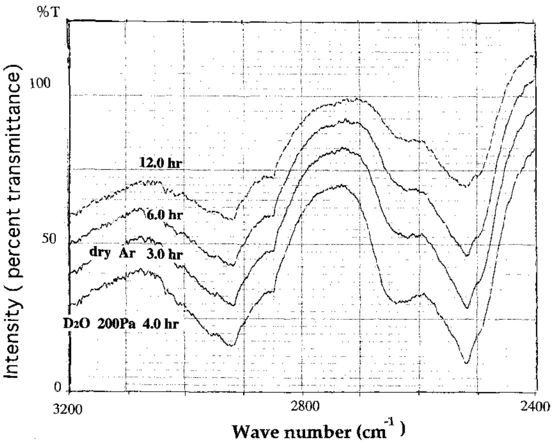

Fig. 3. Absorption spectra of Li_2O during drying under dry Ar at 833 K.

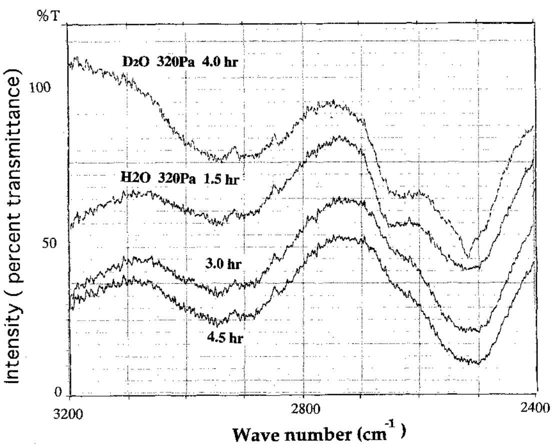

Fig. 5. Absorption spectra of Li_2O when sweep gas was changed from Ar + D_2O to Ar + H_2O.

various temperatures up to 973 K. The spectra was measured after at least 12 h at each temperature. In Fig. 4, a sample dried at 973 K was used as reference. Intensities of these bands decreased with increasing temperature, and they disappeared while drying at 973 K for more than 12 h under dry Ar atmosphere. This means that a considerable amount of surface –OD could exist below 973 K under Ar atmosphere and these –ODs were desorbed through a recombination reaction above 973 K. At 973 K, all the hydroxyl groups remaining on the surface at lower temperatures were considered to be completely removed.

Figs. 5 and 6 show the absorption spectra of an Li_2O sample when the sweep gas was changed from Ar + D_2O (320 Pa) to Ar + H_2O (320 Pa) or Ar + H_2 (3400 Pa) respectively. Both adsorption and desorption was conducted at 833 K. In both cases, surface –ODs, attributed to peaks at 2660 and 2520 cm^{-1} were removed within 3 h and corresponding surface –OH peaks to the surface –OD peaks were observed at 3600 and 3400 cm^{-1}. Peaks at 2900, 2540 and 2490 cm^{-1} could not be removed by H_2O addition in 24 h. However, under the H_2 containing atmosphere, these peaks vanished after 24 h. In this case, corresponding surface –OH peaks could not be observed, indicating that this reaction is not the exchange or substitution reaction. From these observations, the surface –OD was considered to be removed by a recombination reaction with adjacent surface –OH produced by dissociative adsorption of H_2 on the surface.

We also observed the change of adsorption spectra when the sweep gas was changed from Ar + D_2 to Ar + H_2O or Ar + H_2 (Fig. 7). Under the D_2 atmosphere, three peaks were observed at 2900, 2540, and 2490 cm^{-1} (Fig. 2). However the surface –OD could not be removed by adding both H_2 and H_2O to the atmosphere in 24 h. This observation indicates that when the sample was pre-treated

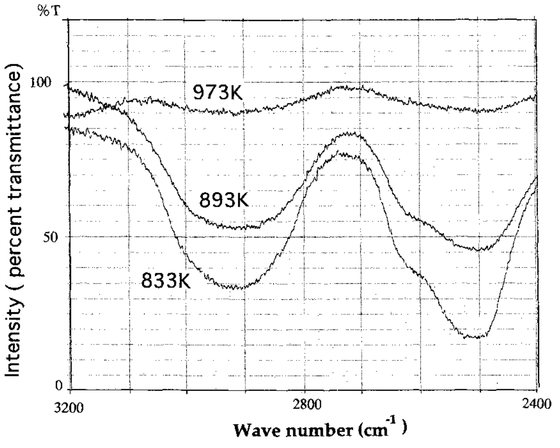

Fig. 4. Absorption spectra of Li_2O during drying up to 973 K.

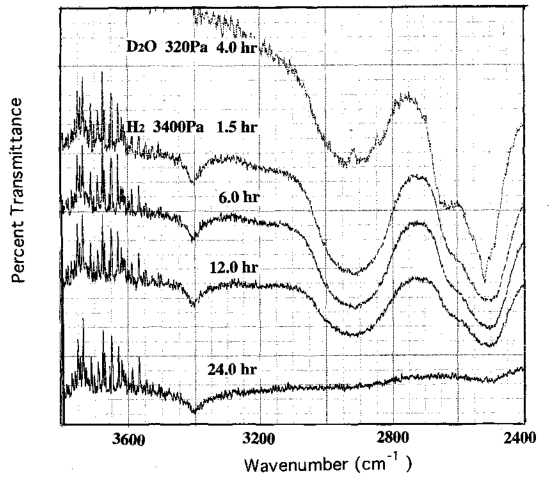

Fig. 6. Absorption spectra of Li_2O when sweep gas was changed from Ar + D_2O to Ar + H_2.

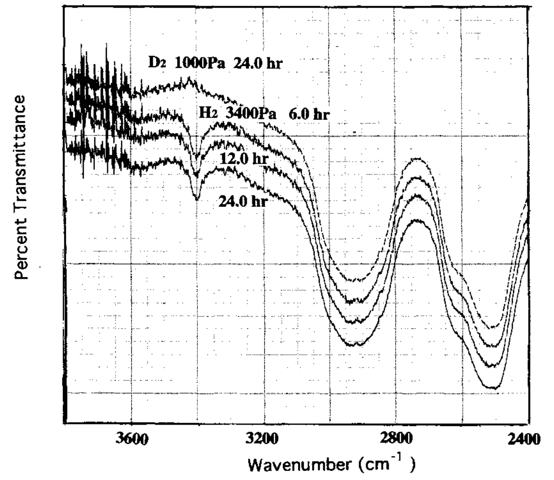

Fig. 7. Absorption spectra of Li_2O when sweep gas was changed from $Ar + D_2$ to $Ar + H_2$.

with D_2, H_2 or H_2O molecules, it is hard to be adsorbed on sites adjacent to –ODs attributed to 2900, 2540 and 2490 cm^{-1}. It also appears that desorption of HDO by a recombination reaction is hard to take place for these surface –OD sites.

3. Comparison of the results of FT-IR study with those of in situ tritium release experiments (TTTEx)

From the results of our in situ tritium release experiments (TTTEx), it was observed that the tritium release rate was enhanced by adding H_2 or H_2O to the sweep gas [3]. This tendency could be reasonably explained from the results of the FT-IR study. It was observed that the disappearance of the peaks at 2660 and 2520 cm^{-1} was faster when H_2 or H_2O was added to the sweep gas than when dry Ar was used as the sweep gas (Figs. 3 and 5). This observation suggests that added H_2 or H_2O enhances the desorption of –OD on the surface. Surface –OD corresponding to the peak at 2660 cm^{-1} was observed only under high D_2O vapor pressure and was assigned to –OD with many –ODs as a neighbor. The peak at 2520 cm^{-1} was observed mainly under a D_2O atmosphere and assigned to surface –OD on an active site like corner or edge in the crystal. Under those conditions, H_2O or H_2 adsorption on adjacent sites to this –OD is considered to be easy. Therefore, desorption of tritium trapped at these sites is considered to be enhanced under H_2O or H_2 containing atmosphere because dissociative adsorption of H_2 or H_2O enhances the recombination reaction of –OT and –OH as HTO causing the improvement of tritium release.

In TTTEx, it was observed that the oxygen partial pressure near the Li_2O sample was decreased by adding the hydrogen to the sweep gas of N_2. Under this condition, the concentration of the oxygen ion on the surface of Li_2O sample is considered to be relatively low. Tritium release was faster for the sample pre-treated by H_2 containing sweep gas (low oxygen concentration) than that pre-treated by N_2 gas (relatively high oxygen concentration). Also in this work, it was observed that the chemical form of the recovered tritium has a strong relationship with the oxygen partial pressure near the surface.

A similar tendency was also observed in –OD desorption experiments using FT-IR. Under the H_2 atmosphere, surface –OD, attributed to peaks at 2540 and 2490 cm^{-1} could be removed only when the sample was pre-treated under D_2O atmosphere. On the contrary, when the sample was treated by a D_2 containing atmosphere, surface –OD could not be removed by $Ar + H_2$ sweep gas (Section 2.3). Surface –OD corresponding to peaks at 2540 and 2490 cm^{-1} are thought to be surface isolated –OD which have a small number of O^{2-} in the neighborhood because they were observed only under the D_2 atmosphere in which the oxygen concentration on the surface is relatively low [6]. Therefore, adsorption of –OH in an adjacent site is required in order to remove these hydroxyl groups by recombination reactions. However, when a sample was pre-treated with D_2 containing sweep gas, the oxygen concentration of the surface is relatively low. Under this condition, dissociative adsorption of H_2 on the surface is considered to be difficult because dissociative adsorption of H_2 requires two neighboring oxygen ions on the surface. Therefore, recovery of these –OTs needs an exchange reaction. From the discussion above, we can conclude qualitatively that the desorption behavior of surface –OT varies according to the adsorption site which is affected by the chemical composition of the sweep gas.

4. Conclusions

Absorption spectra from –OH and –OD on the surface of Li_2O were studied by using diffuse-reflectance Fourier transform infrared spectroscopy under controlled atmosphere and temperature up to 973 K. The following conclusions were obtained by FT-IR observation.

It was observed that hydroxyl groups of peaks at 2900, 2540 and 2490 cm^{-1} could exist on a Li_2O surface up to 973 K under Ar atmosphere. In order to remove these –ODs at 833 K, addition of H_2 to the sweep gas was needed.

The enhancement of desorption of surface –OD was confirmed when H_2 or H_2O was added to the sweep gas especially for the surface –OD corresponding to peaks at 2660 and 2520 cm^{-1}. It was also observed that the desorption behavior of surface –OD to the sweep gas of $Ar + H_2$ was influenced by the oxygen partial pressure near the sample. These facts are consistent with the results of in situ tritium release experiments.

References

[1] S. Tanaka, A. Kawamoto, D. Yamaki, K. Yamaguchi, M. Yamawaki, J. Nucl. Mater. 179–181 (1991) 867.

[2] W. Breitung, H. Werle, J. Nucl. Mater. 179–181 (1991) 847.

[3] M. Taniguchi, S. Tanaka, V. Grishmanov, Fusion Technol. 28 (1995) 1284.

[4] D. Yamaki, S. Tanaka, M. Yamawaki, J. Nucl. Mater. 191–194 (1992) 204.

[5] S. Tanaka, M. Taniguchi, M. Nakatani, D. Yamaki, M. Yamawaki, J. Nucl. Mater. 218 (1995) 335.

[6] M. Taniguchi, S. Tanaka, Y. Nose, Fusion Technol. 28 (1995) 1284.

[7] M. Taniguchi, S. Tanaka, Fusion Technol., in press.