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Improvement of the model for surface process of tritium release from lithium oxide

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Abstract

Among the various tritium transport processes in lithium ceramics, the importance and the detailed mechanism of surface reactions remain to be elucidated. The dynamic adsorption and desorption model for tritium desorption from lithium ceramics, especially Li_2O was constructed. From the experimental results, it was considered that both H_2 and H_2O are dissociatively adsorbed on Li_2O and generate OH^- on the surface. In the first model developed in 1994, it was assumed that either the dissociative adsorption of H_2 or H_2O on Li_2O generates two OH^- on the surface. However, recent calculation results show that the generation of one OH^- and one H^- is more stable than that of two OH^-s by the dissociative adsorption of H_2. Therefore, assumption of H_2 adsorption and desorption in the first model is improved and the tritium release behavior from Li_2O surface is evaluated again by using the improved model. The tritium residence time on the Li_2O surface is calculated using the improved model, and the results are compared with the experimental results. The calculation results using the improved model agree well with the experimental results than those using the first model. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Estimation of the precise tritium inventory in the fusion reactor blanket and the chemical form of the released tritium are essential for the effective recovery of tritium in the fusion reactor fuel cycle. To estimate the tritium inventory in the blanket system and the chemical form of the released tritium, a thorough understanding of tritium release behavior from breeding materials is required. In sintered solid breeding materials, tritium release is composed of a series of migration steps. Among them, surface reactions are known to be important.

Computer modeling is an important tool for clarifying the mechanism of surface reaction in the tritium release process and for estimating tritium inventory in the blanket and the chemical form of the released tritium [1–5]. The DAD (the dynamic adsorption and desorption) model was developed in 1994 to describe the surface processes of tritium release from Li_2O and was used to estimate the tritium inventory on the surface and the chemical form of the released tritium [6]. From the results of in situ tritium release experiments (TTTEx), it was clarified that tritium release rate from the Li_2O surface is affected both by the swamping effect with H_2 and H_2O and by the surface oxygen potential effect [7]. To describe both effects, the first DAD model developed in 1994 assumed that the surface is covered with hydroxyl ions, oxygen ions and vacancies on interstitial and lattice sites, that is, the swamping effect is considered to be described as the fraction of hydroxyl ions and the oxygen potential effect as the unbalance between the fraction of oxygen ions and vacancies.

In the first DAD model, the fractions of these species are determined from the partial pressures of H_2 and H_2O in the sweep gas by adsorption and desorption reactions of H_2 and H_2O. Tritium is released by three processes: as HTO by recombination of OH^- and OT^- on the surface, as HT by recombination of OH^- and OT^- at low oxygen potential or when these surface groups are surrounded by 'active' oxygen vacancies, and as HT by exchange reaction of surface OT^- with H_2 in

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the gaseous phase. However, by the recent calculation results [8], it is clarified that the assumption of the H_2 adsorption and desorption processes in the DAD model is not suitable for describing the tritium release surface processes.

In the present study, the DAD model is improved by introducing the new assumption for H_2 adsorption and desorption process founded on the recent calculation results. The dependencies of the fraction of surface adsorbed species and the surface tritium residence time on the sweep gas chemical form are calculated, using the 'improved' DAD model, and the calculation results are compared with the experimental results.

2. Improvement of the model

In the DAD model, the (1 1 0) surface of Li_2O was selected for modeling. On the ideal (1 1 0) surface, as shown in the top three rows of Fig. 1, O^{2-} on the O^{2-} lattice sites and empty site (E_O) located on the interstitial sites of the O^{2-} sub-lattice are arranged regularly among the Li^+ lattice. These two kinds of sites will become the sites for OH^- adsorption (O_{ads} site in Fig. 1). Strictly speaking, E_O (empty site on interstitial sites of O^{2-} sub-lattice) and V_O (vacancy on O^{2-} lattice sites) are energetically different. However, it is considered that the surface species, OH^- and O^{2-}, can occupy both the lattice and the interstitial sites because OH^- and O^{2-} can move easily on the surface. Therefore, at the surface, it is considered that there is no significant difference in the energetics between the E_O on the interstitial site and the V_O on the lattice site. Therefore, in the DAD model, for simplification of the model calculation, E_O and V_O are treated equally as a kind of oxygen vacancy at the surface. The symbol V_S is used for such an oxygen vacancy at the surface, including both E_O and V_O.

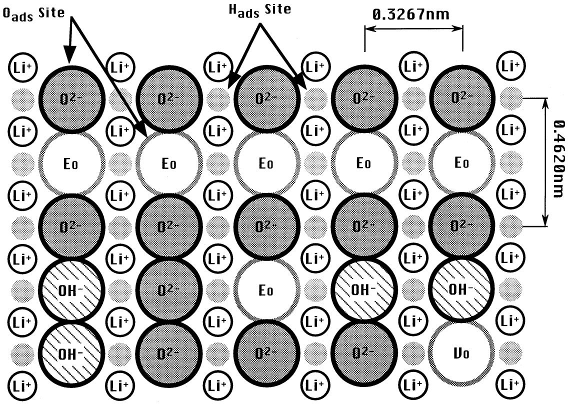

Fig. 1. The (1 1 0) surface of the Li_2O crystal. OH^-s are absorbed partially.

In the first DAD model, H_2O and H_2 adsorption and desorption processes were assumed to be as follows [6]: H_2O is dissociatively adsorbed on two adjacent O_{ads} sites occupied by one V_S and one O^{2-}, and then produces two OH^-s. H_2 is dissociatively adsorbed on two adjacent O_{ads} sites occupied by two O^{2-}s and produces two OH^-s. H_2O is desorbed from two adjacent O_{ads} sites occupied by two OH^-s by recombination process leaving V_S and O^{2-}. When the surface oxygen potential is very low, V_S existing on the adjacent sites of OH^-s are considered to affect the nature of OH^-s. Such V_S which we named active oxygen vacancy (V_O^a) was considered to attract the oxygen atoms of OH^-s to the surface and the recombined OH^-s were considered to be desorbed as H_2.

The calculation results of the surface tritium residence time by using the first DAD model showed good agreement with the results of the in situ experiments [6]. However, some issues were pointed out in the assumptions in the first model. It seemed that electric balance was not maintained before and after the H_2 adsorption, $H_2 + 2O^{2-} \rightarrow 2OH^-$. In addition, the definition of active oxygen vacancy which plays an important role in H_2 desorption was not clear. These issues remained to be improved founded on the detailed study on the adsorption and desorption mechanism of H_2.

Recently, Taniguchi et al. performed the quantum chemical calculations to simulate the dissociative adsorption of H_2 on the Li_2O surface [8]. They estimated the heat of H_2 dissociative adsorption on the three types of possible adsorption sites. The three sites were as follows: (1) two dissociative H atoms are adsorbed on two O^{2-} and produce two hydroxyl ions, same as the assumption in the first DAD model, (2) one dissociative H atom is adsorbed on O^{2-} to produce OH^- and another dissociative H atom is adsorbed on the nearest Li^+, and (3) one dissociative H atom is adsorbed on O^{2-} to produce OH^- and another dissociative H atom is adsorbed on the site existing between the two nearest lithium ions (H_{ads} site in Fig. 1). Their calculation results showed that the last adsorption site is the most stable site for dissociative adsorption of H_2 on Li_2O.

Based on these calculation results, the alternation of the assumption of H_2 adsorption and desorption mechanism in the first DAD model is performed, and the improved DAD model was constructed. In the first model, only O_{ads} sites in Fig. 1 were considered as the dissociative adsorption sites for H_2 and H_2O. In the improved model, H_{ads} sites in Fig. 1 are also considered as the dissociative adsorption sites for H_2.

The assumption of the H_2 and H_2O adsorption and desorption mechanisms in the improved model is as follows: H_2O adsorption and desorption are assumed to occur on the O_{ads} sites in the same process as assumed in the first model. H_2 is assumed to be dissociatively adsorbed on O^{2-} and adjacent E_H (H_{ads} site which is not occupied by H^-) and produces OH^- and H^-. When OH^- does not have any neighboring OH^- and has adjacent H^- on the nearest H_{ads} site, H_2 is assumed to be desorbed by recombination process of OH^- and H^- and leaves O^{2-} and E_H.

3. Calculation

The H_2O adsorption rate is calculated as follows: (1) The probability of O_{ads} site occupied by a V_S which has a neighboring O^{2-} or by O^{2-} which has a neighboring V_S is $\theta_V[1-(1-\theta_O)^2]+\theta_O[1-(1-\theta_V)^2]$, where θ_V and θ_O are the surface coverages of V_S and O^{2-} on O_{ads} sites, respectively. (2) As the H_2O adsorption rate should be proportional to the H_2O pressure in the gaseous phase near the surface, the H_2O adsorption rate on the pair of sites occupied by a V_S and O^{2-} is described as $K^a_{H_2O}\{\theta_V[1-(1-\theta_O)^2]+\theta_O[1-(1-\theta_V)^2]\}P_{H_2O}$, where $K^a_{H_2O}$ (molecules Pa^{-1} s^{-1} site^{-1}) is the rate constant H_2O adsorption and P_{H_2O}(Pa) the partial pressure of H_2O. (3) The number of the O_{ads} sites on the Li_2O surface is equal to $N_{SO}A$, where N_{SO} (sites m^{-2}) is the area density of O_{ads} sites and A (m^2) is the surface area of Li_2O. Then, the overall H_2O adsorption rate $R^a_{H_2O}$ (molecules s^{-1}) is

$$R^a_{H_2O}=K^a_{H_2O}\{\theta_V[1-(1-\theta_O)^2] + \theta_O[1-(1-\theta_V)^2]\}P_{H_2O}N_{SO}A. \qquad (1)$$

The overall H_2 adsorption rate $R^a_{H_2}$ (molecules s^{-1}) is calculated in the same way as the H_2O adsorption,

$$R^a_{H_2}=K^a_{H_2}\theta_O[1-(1-\theta_{EH})^2]P_{H_2}N_{SO}A, \qquad (2)$$

where $K^a_{H_2}$ (molecules Pa^{-1} s^{-1} site^{-1}) is the rate constant of H_2 adsorption, θ_{EH} the surface coverage of E_H on H_{ads} sites and P_{H_2} (Pa) is the partial pressure of H_2.

Since the probability of one pair of neighboring O_{ads} sites being occupied by two OH^- is $\theta_{OH}[1-(1-\theta_{OH})^2]$, the overall H_2O desorption rate $R^d_{H_2O}$ (molecules s^{-1}) is described as

$$R^d_{H_2O}=K^d_{H_2O}\theta_{OH}[1-(1-\theta_{OH})^2]N_{SO}A, \qquad (3)$$

where $K^d_{H_2O}$ (molecules s^{-1} site^{-1}) is the rate constant of H_2O desorption and θ_{OH} the surface fraction of OH^- on O_{ads} sites.

The overall H_2 desorption rate $R^d_{H_2}$ (molecules s^{-1}) is calculated in the same way as the H_2O desorption,

$$R^d_{H_2}=K^d_{H_2}\theta_{OH}[1-(1-\theta_H)^2](1-\theta_{OH})^2N_{SO}A, \qquad (4)$$

where $K^d_{H_2}$ (molecules s^{-1} site^{-1}) is the rate constant of H_2 desorption and θ_H is the surface coverage of H^- on H_{ads} sites.

The relation among the surface coverages is expressed by

$$\begin{aligned}&\theta_O+\theta_V+\theta_{OH}=1,\quad \theta_H+\theta_{EH}=1,\quad 0<\theta_O<1,\\ &0<\theta_V<1,\quad 0<\theta_{OH}<1, \qquad (5)\\ &0<\theta_H<1,\quad 0<\theta_{EH}<1.\end{aligned}$$

On the ideal (1 1 0) surface of Li_2O which absorbs neither hydrogen nor hydroxyl groups, the relations of $\theta_v=\theta_O$ and $\theta_H=0$ are established. In the improved model assumption, H^- on H_{ads} sites increases and O^{2-} on O_{ads} sites decreases by the adsorption of H_2 molecule. Also, H^- on H_{ads} site decreases and O^{2-} on O_{ads} site increases by the desorption of H_2 molecule. The relation of $\theta_v=\theta_O$ and the value of θ_H does not change by the adsorption and desorption of H_2O. As shown in Fig. 1, N_{SH} is equal to N_{SO}. Therefore, the relation of $\theta_H+\theta_O=\theta_v$ is established on the ideal (1 1 0) surface in the H_2 and H_2O adsorption and desorption system.

When the equilibrium state of H_2O adsorption and desorption is established, from Eqs. (1) and (3),

$$K^a_{H_2O}\{\theta_V[1-(1-\theta_O)^2]+\theta_O[1-(1-\theta_V)^2]\}P_{H_2O} - K^d_{H_2O}\theta_{OH}[1-(1-\theta_{OH})^2]=0 \qquad (6)$$

When the equilibrium state of H_2 adsorption and desorption is established, from Eqs. (2) and (4),

$$K^a_{H_2}\theta_O[1-(1-\theta_{EH})^2]P_{H_2}-K^d_{H_2}\theta_{OH}[1-(1-\theta_H)^2] \times(1-\theta_{OH})^2=0 \qquad (7)$$

Tritium generated in Li_2O is considered to exist as OT^- on O_{ads} sites or T^- on H_{ads} sites by exchange reaction. In the improved model, it is assumed that the ratio of OT^-/T^- on Li_2O surface is equal to that of OH^-/H^- on the surface.

When the surface density of tritium is much less than that of hydrogen, tritium on the surface is considered to be released as HTO by recombination of surface OH^- and OT^-, and HT by recombination of surface OH^- and T^-, or OT^- and H^-, which are the similar processes to the desorption of H_2O or H_2. Moreover, from the in situ experimental results, HT is also considered to be released by the exchange reaction between H_2 in the sweep gas and OT^- or T^- on the surface [7]. In this improved model, it is assumed that the HT is released by the exchange reaction from OT^- which has no OH^- on its adjacent O_{ads} sites and no H^- on its adjacent H_{ads} sites, and from T^- which has no OH^- on its adjacent O_{ads} sites. Therefore, the total tritium release rate R_T is described as

$$\begin{aligned}R_T={}&K^r_{HTO}\theta_{OT}[1-(1-\theta_{OH})^2]N_{SO}A\\ &+K^r_{HT}\{\theta_{OT}[1-(1-\theta_H)^2](1-\theta_{OH})^2\\ &+\theta_T[1-(1-\theta_{OH})^2]\}N_{SO}A\\ &+K^e_{HT}[\theta_{OT}(1-\theta^2_{OH})N_{SO}A\\ &+\theta_T(1-\theta^2_{OH})(1-\theta^2_H)N_{SH}A]P_{H_2}, \qquad (8)\end{aligned}$$

where K^{r}_{HTO} (molecules s^{-1} site^{-1}), K^{r}_{HT} (molecules s^{-1} site^{-1}) and K^{e}_{HT} (molecules Pa^{-1} s^{-1} site^{-1}) are the release rate constants of HTO by recombination, HT by recombination and HT by exchange reaction, respectively, R_T (molecules s^{-1}) the overall tritium release rate, θ_{OT} is the surface fraction of OT$^-$ on O_{ads} sites, and θ_T is the surface fraction of T$^-$ on H_{ads} sites. The surface tritium residence time τ_T (s) is

$$\tau_T = (\theta_{OT}N_{SO} + \theta_T N_{SH})A/R_T. \tag{9}$$

The kinetic constants in the improved model are determined by comparing with in situ and out-of-pile experiments at 773 K.

When no H_2 exists in the gaseous phase, the relation of $\theta_{OH} = \theta_O$ and $\theta_H = 0$ is established, and Eqs. (6) and (8) are simplified. K^{r}_{HTO} is considered to be nearly equal to $K^{d}_{H_2O}$. From Eq. (9) and the simplified Eqs. (6) and (8), $K^{d}_{H_2O}(K^{r}_{HTO})$ and $K^{a}_{H_2O}$ were calculated to be 1.7×10^{-2} (molecules s^{-1} site^{-1}) and 1.9×10^{-5} (molecules Pa^{-1} s^{-1} site^{-1}), respectively, by using experimental data for the tritium surface residence time for the He + H_2O sweep gas [7] and the amount of H_2O adsorption on Li_2O [9].

It is not easy to determine $K^{d}_{H_2}$ and $K^{a}_{H_2}$ only from in situ or out-of-pile experiments because at actual conditions the experimental result is inevitably affected by coexisting H_2O. In the improved model, their values are determined from the balance between θ_O and θ_V, which is the similar process of evaluation in the first DAD model. For the condition in which P_{H_2O} is much larger than P_{H_2}, θ_V is considered to be nearly equal to θ_O, because the surface balance is mainly determined by the adsorption and desorption of H_2O. If the effect of H_2 becomes significant, imbalance occurs between θ_V and θ_O. In the improved model, it has been assumed that the imbalance between θ_V and θ_O begins at $P_{H_2O} = 100$ Pa and $P_{H_2} = 1$ Pa, which is the same assumption as in the first model [6]. It led to $K^{d}_{H_2} = 2.0\times10^{-4}$ (molecules s^{-1} site^{-1}) and $K^{a}_{H_2} = 9.5\times10^{-7}$ (molecules Pa^{-1} s^{-1} site^{-1}) by using experimental data for the tritium surface residence time for the He + H_2 + H_2O sweep gas [10].

K^{r}_{HT} is considered to be nearly equal to $K^{d}_{H_2}$, so $K^{r}_{HT} = 2.0\times10^{-4}$ (molecules s^{-1} site^{-1}).

K^{e}_{HT} is calculated from the results of in situ experiments of the sample at low oxygen potential, where tritium surface residence time was found to be inversely proportional to the hydrogen pressure, to be 6.0×10^{-5} (molecules s^{-1} site^{-1}).

4. Results and discussions

Fig. 2 shows the surface coverages of OH$^-$, O^{2-} and V_S on O_{ads} sites. In the calculation results using the first DAD model, large imbalance appears between θ_O and θ_V even in the region for which P_{H_2O} is much larger than P_{H_2}. However, using the improved DAD model, no imbalance appears between θ_O and θ_V in the region for which P_{H_2O} is much larger than P_{H_2} (see Fig. 2). This result shows that the assumed mechanism of H_2 adsorption and desorption in the improved model is more adequate for evaluating the tritium behavior on Li_2O surface than that in the first model.

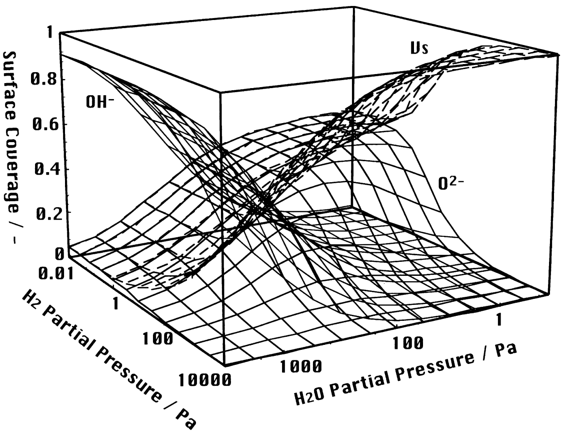

Fig. 2. Calculated surface coverages on O_{ads} sites.

Fig. 3 shows the calculated surface tritium residence time using the improved model compared with the experimental results from TTTEx [10]. Characteristics of model calculation are as follows: (1) τ_T is inversely proportional to P_{H_2} at low P_{H_2O}, (2) inversely proportional to the square root of P_{H_2O} at low P_{H_2}, and (3) has a ridge on the line where P_{H_2O} is nearly equal to P_{H_2}. These characteristics of the calculated results agree well with the experimental results, and the estimated values of τ_T

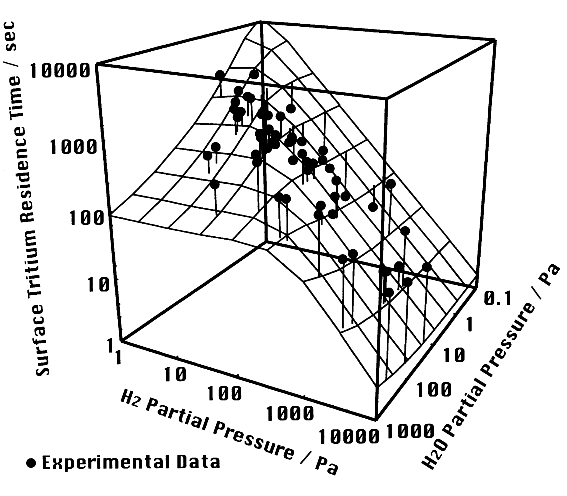

Fig. 3. Calculated surface tritium residence time compared with the experimental data from TTTEx [10].

agree more satisfactorily with the experimental results than the first DAD model, especially in the regions of $P_{H_2} \leqslant 500$ Pa and $P_{H_2O} \leqslant 100$ Pa [6]. However, there is a tendency for the difference between the experimental and calculated to become larger in a higher P_{H_2} region, same as with the first DAD model. A possible explanation for this tendency is the large experimental error due to the small residence time, or that the equilibrium on the surface is not established in higher P_{H_2} region.

5. Conclusion

The DAD model, which explains both the effects of swamping with hydrogen isotopes and the surface oxygen potential on tritium release from the Li_2O surface, is improved according to the recent calculation results performed by Taniguchi et al. The results of this improved DAD model show better agreement with the data from in situ experiments (TTTEx) than the first DAD model.

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