Isotope exchange reaction between tritiated water and hydrogen on SiC

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Abstract

SiC has been considered as a primary candidate material for a first wall component in future fusion reactor because it has been claimed that SiC has excellent high-temperature properties, good chemical stability and low activation. However, the behavior of tritium on SiC has not been discussed yet. In this study, tritium trapping capacity on the surface of SiC was experimentally obtained at the temperature range of 25–800 °C in consideration of tritium trapping to the experimental system. The capacity, which was independent of the water vapor pressure in the gas phase and the temperature, was determined as about 10^6 Bq/cm². The isotope exchange reaction rate between tritiated water in a gas phase and hydrogen on the surface was quantified at the temperature of 25, 500 and 700 °C in consideration of the behavior of tritium trapping at change of experimental condition by the numerical curve fitting method applying the serial reactor model. The reaction rate was observed to be constant as 3.48×10^{-5} m/s. Additionally tritium release behavior from the surface of SiC in water vapor atmosphere was predicted and compared with that for graphite and stainless steel.
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1. Introduction

After D–T campaign in the Tokamak fusion reactor (TFTR) and Joint European Torus (JET), vacuum vessel purges with air have been performed [1,2]. These results indicate that an air purge is effective on tritium elimination from the surface of first wall. It has been revealed that non-negligible amount of tritium is tenaciously held on the surface even after several decontamination processes. In addition, the rapid progress of the isotope exchange reaction between water vapor in air and tritium on the wall surface has been confirmed. Also

when pure deuterium fuel was injected into plasma after D–T experiment in JET, it was observed that the value of tritium fraction $T/(T + D)$ in plasma increased [2]. This phenomenon can be explained by the isotope exchange reaction between deuterium in the gas phase and tritium remains on the wall surface. Thus, the isotope exchange reaction is close relation to tritium behavior in every case when tritium contacts with hydrogen isotopes or water vapor on material surface, for example in fuel injection, plasma discharge, decontamination, and decomposition of the reactor. Accordingly, it is necessary to understand the isotope exchange reaction on candidate materials for first wall components.

SiC has been considered as a primary candidate material for a first wall component in future fusion reactor because it has been claimed that SiC has excellent high-temperature properties, good chemical stability and low activation. Thus far hydrogen retention, release behavior or reduction of chemical erosion for several SiC materials such SiC/SiC composite, Si-doped carbon,

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amorphous SiC or siliconized first wall has been investigated [3–8]. However, the behavior of tritium on SiC has not been sufficiently discussed yet. We have already reported for the isotope exchange reaction between deuterium and hydrogen on SiC surface [9]. In this study, tritium trapping capacity on the surface of SiC is experimentally obtained at the temperature range of 25–800 °C. Additionally, the rate of the isotope exchange reaction between tritiated water in a gas phase and hydrogen on the surface is quantified at the temperature of 25, 500 and 700 °C by the numerical curve fitting method applying the serial reactor model. Moreover, tritium release behavior from the surface of SiC in water vapor atmosphere is predicted and compared with that for graphite and stainless steel.

2. Theoretical background

When the behavior of tritium is experimentally investigated, it must be taken into consideration that interactions between tritium and the system materials affect the behavior of tritium in the system. Because tritium is apt to be trapped to the surfaces of the subsystems by such reactions as adsorption, absorption, and isotope exchange reactions. This phenomenon has been named as the system effect by the present authors [10]. The system effect is classified into static system effect and kinetic system effect. The former represents the total amount of tritium trapped to the surface of system materials and the latter represents the synthetic result of kinetic behavior of tritium in the subsystem that compose the whole system.

It is considered by the present authors that some amount of chemical groups such as –H bases or –O–H bases exist on the surface of ceramic breeder materials [11,12], metals [13] or graphite [14]. When the molecular form of tritium (HT or T_2) is present in a gas phase, the isotope exchange reaction between tritium in the gas phase and hydrogen on the surface (named the isotope exchange reaction (1) by the present authors) supplies tritium to the surface until the H/T ratio on the surface becomes the same as the H/T ratio in the gas phase:

Isotope exchange reaction (1)

$$T_2(\text{gas phase}) + 2(-H)(\text{surface})$$
$$\Longleftrightarrow H_2(\text{gas phase}) + 2(-T)(\text{surface}) \qquad (1)$$
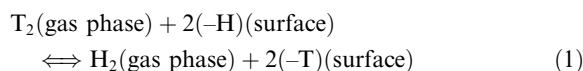
When tritiated water (HTO or T_2O) is present in a gas phase, the isotope exchange reaction between tritiated water in the gas phase and hydrogen on the surface (named the isotope exchange reaction (2)) supplies tritium to the surface until the H/T ratio on the surface becomes the same as the H/T ratio in the gas phase:

Isotope exchange reaction (2)

$$T_2O(\text{gas phase}) + 2(-H)(\text{surface})$$
$$\Longleftrightarrow H_2O(\text{gas phase}) + 2(-T)(\text{surface}) \qquad (2)$$
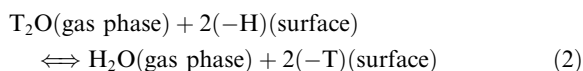
In this study, overall mass transfer coefficient representing the isotope exchange reaction (2) is quantified.

3. Experimental

The sample used in this experiment is SiC (SC-20 by NGK Insulators, Ltd.), which is made by sintering in argon atmosphere at temperature of 2200 °C. SiC was crushed into granules with 12–16 mesh and then packed in a quartz reaction tube. Each granule of SiC seems to be a single crystal because the boundary of crystal grain has not been observed clearly with SEM image shown in Fig. 1. Specifications of sample and experimental conditions are shown in Table 1.

Tritium trapping capacity on the surface of SiC was quantified by the breakthrough method using tritiated water in nitrogen gas flow. The tritium trapping capacity is obtained from the sum of adsorption capacity and
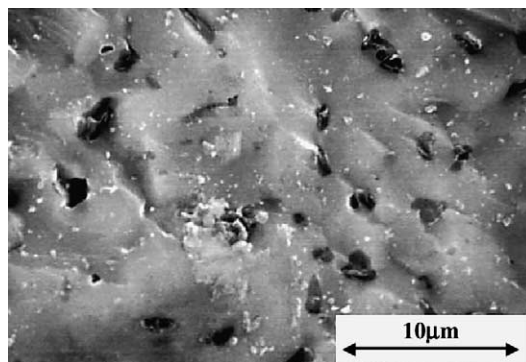

Fig. 1. SEM image of SiC used in this study.

Table 1
Specifications of sample and experimental conditions

SiC (SC-20)	
Sample weight (g)	23.5
Granule size (mesh)	12–16
Height of packed bed (mm)	35.90
Inner diameter of reaction tube (mm)	25.4
Void fraction of packed bed (–)	0.59
Specific surface area of bed (m^2/m^3)	2.04×10^3
Gas flow rate (ml/min)	200
Temperature of sample bed (K)	298–1073
Concentration of Tritium (Bq/cm^3)	1841–4794
Partial pressure of H$_2$O (Pa)	6–112
H/T ratio (–)	1592–45 340

isotope exchange capacity. The adsorption capacity was investigated from the amount of tritiated water released from the surface during the purging procedure by the dry nitrogen gas following the trapping of water or tritiated water at the same temperature. Subsequently, the amount of residual tritium tenaciously held on the surface was investigated from the amount of tritiated water released from the surface during the purging procedure by the nitrogen gas containing water vapor. This amount represents the isotope exchange capacity. Experimental apparatus and procedures have been stated in detail in the previous paper [15]. The sample bed system of this apparatus consists of copper pipes, a quartz tube with brass joint, and an ionization chamber with copper electrodes.

The rate of the isotope exchange reaction was quantified from analyzing the transitional response curve of tritium at the outlet of the experimental apparatus. The numerical curve fitting was performed applying the serial reactor model at the temperature of 25, 500 and 700 °C. The theory to quantify the mass transfer coefficient was stated in detail in the previous paper [10].

4. Results and discussion

4.1. Tritium trapping capacity

Lines in Fig. 2 show the amount of tritiated water released from the surface of system materials by the dry gas purge, which were previously estimated from blank test. Symbols in this figure show the amount of the tritiated water released from SiC surface and the system
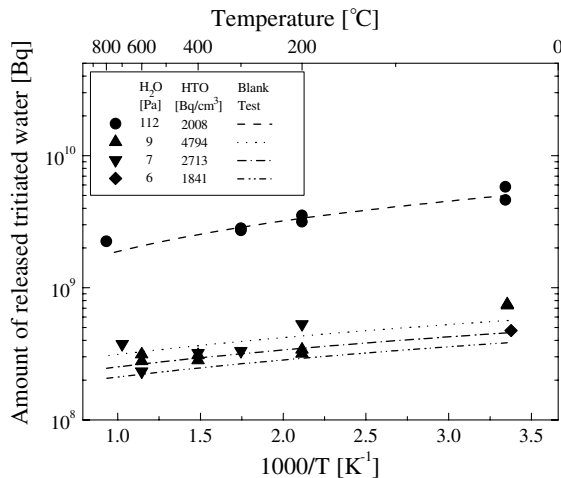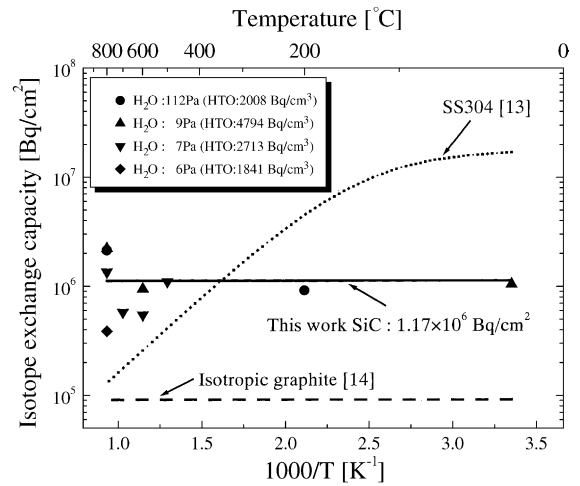
Fig. 3. Comparison of the isotope exchange capacity on SiC with that on graphite and stainless steel.

material surfaces by the dry gas purge. As can be seen in Fig. 2, the experimental values are in agreement with the values estimated from blank test. Therefore it could be said that most of the released tritium was trapped on the system material surfaces. This indicates that SiC has almost no adsorption capacity for water vapor while the system materials have adsorption capacity.

Fig. 3 shows the comparison of the isotope exchange capacity on SiC with that on graphite [14] or SS304 with mirror-finished surface [13]. We could be experimentally ascertained that tritium remains on SiC surface even after the purging procedure by the dry gas at so high-temperature and the residual tritium can be easily released by the isotope exchange reaction between water vapor in a gas flow.

The isotope exchange capacity on SiC is observed to be independent of the water vapor pressure and the temperature, similarly to graphite, though that on stainless steel decreases as the temperature increases. The average value of the isotope exchange capacity is obtained as 1.17×10^6 Bq/cm^2 at the temperature range of 25–800 °C. It is found that SiC has no adsorption capacity and the largest isotope exchange capacity among three materials at above 400 °C.

4.2. Rate of isotope exchange reaction (2)

The tritium trapping capacities and the overall mass transfer coefficients of the isotope exchange reaction (2) on system materials, which are copper, quartz and brass, must be previously quantified to estimate the system effect. The tritium sorption properties of copper have been already obtained in the previous study [13,16].

Fig. 2. Amount of tritiated water released from SiC sample bed system by the dry gas purge.

The tritium sorption properties of quartz are previously obtained in this work as tritium trapping capacity is $3.74 \times 10^{-13} \exp(3120 \, (J/mol)/RT)$ mol T_2/cm^2, where R is the gas constant (J/mol K) and T is temperature (K), and the overall mass transfer coefficient of the isotope exchange reaction (2) is 1.20×10^{-8} m/s. It is assumed in this work that the tritium sorption property of brass is the same as that of copper.

The detailed diagram of the sample bed system is shown in Fig. 4(a). We modeled that the sample bed system consists of 14 serial flow reactors indicated in Fig. 4(b) according to material and geometric shape. Also it is decided that the type of flow state in upper brass joint and ionization chamber is perfect mixed flow and the others are plug flow. Addition of water vapor shown in this figure was performed to diminish the memory effect [17].

Open circles in Fig. 5 show the example of the response curve from the ionization chamber observed when tritiated water was introduced to SiC sample bed. The broken line in this figure shows the system effect, which is calculated using already obtained data for system materials. Solid curve is numerically estimated applying the serial reactor model to SiC sample bed and piping system. As shown in this figure, the estimated curve agrees well with the experimental values. The area enclosed by the two curves in this figure indicates the isotope exchange capacity on SiC surface. The curve
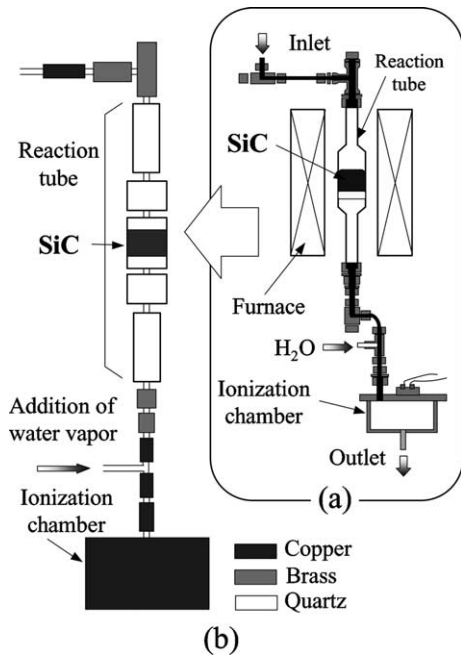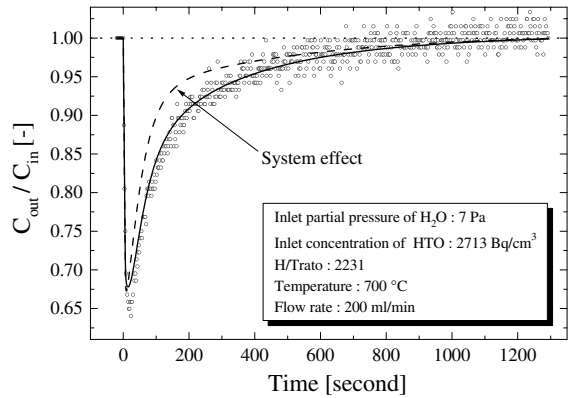

Fig. 5. Example of the response curve from the ionization chamber when tritiated water is introduced to SiC sample bed system. The concentration of tritiated water at the outlet of the sample bed system is normalized by that at the inlet.
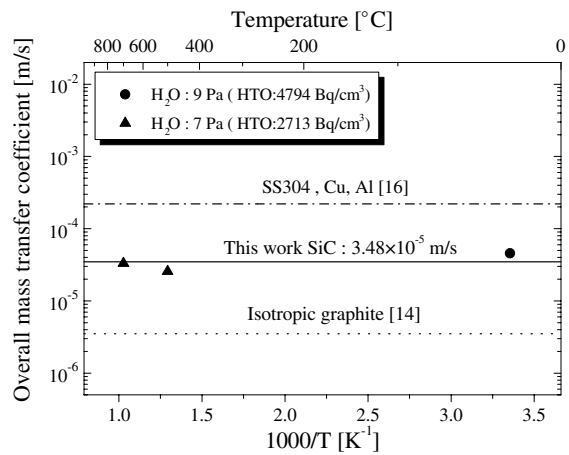

Fig. 6. Comparison of the overall mass transfer coefficient of the isotope exchange reaction (2) on SiC with that on graphite and stainless steel.

Fig. 4. Detailed diagram (a) and serial reactor model (b) of the sample bed system.

fitting method was carried out for the response curve at the temperature of 25, 500 and 700 °C varying the overall mass transfer coefficient as a parameter. The obtained values are shown in Fig. 6 comparing with the values for graphite [14] and metals as stainless steel, copper and aluminum [16]. The overall mass transfer coefficient of the isotope exchange reaction (2) is observed to be constant as 3.48×10^{-5} m/s. The obtained value for SiC is observed to be approximately ten times larger than that for graphite and ten times smaller than that for metal. It is considered from this result that the bonding energy of Si–T is smaller than that of C–T and larger than that of O–T represents structural water on

metal surface such chemically adsorbed water or crystal water.

4.3. Release behavior of tritium

Quantifications of the tritium trapping capacity and the mass transfer coefficient make it possible to predict release behavior of tritium from the surface of SiC placed in water vapor atmosphere. It is shown in Fig. 7 that the change of tritium concentration on the surface of SiC, graphite or stainless steel, where each material is placed in the atmosphere of 10 Pa water vapor after the surface is saturated with tritium at room temperature. It is assumed that the tritiated water adsorbed on the surface of stainless steel has been removed by dry procedures. As can be seen in this figure, tritium concentration on SiC surface reduces until <1 Bq/cm^2 within 10 min. Basically, the tritium removal time using water vapor greatly depends on the initial amount of tritium trapped to the surface of the material because the isotope exchange reaction (2) proceeds rapidly. Accordingly, the tritium removal time for stainless steel is the longest among three materials although the rate of the isotope exchange reaction on stainless steel is the fastest among three materials. Also Fig. 7 shows that the removal time of tritium from stainless steel at 400 °C becomes much shorter than that at room temperature because the isotope exchange capacity for stainless steel decreases as the temperature is heighten. On the contrary, the temperature increase gives no effect on the tritium removal performance by using the isotope exchange reaction (2) for SiC or graphite. Thus, the surface tritium decontamination for SiC requires the longest operation time among three materials under the high-temperature condition although SiC has been expected to use in a high-temperature reactor.
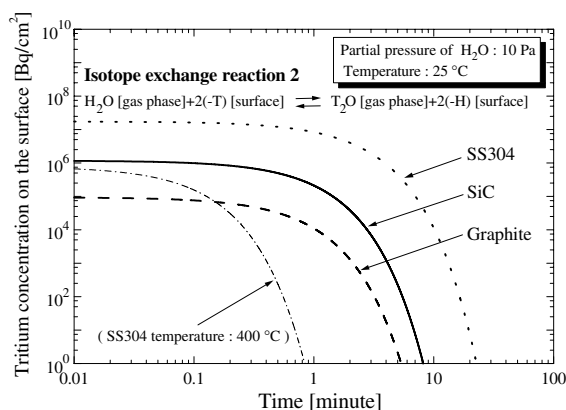

Fig. 7. Comparison of the change of tritium concentration on the surface of SiC with that for graphite or stainless steel.

5. Conclusions

The tritium trapping capacity on the surface of SiC is experimentally obtained as 1.17×10^6 Bq/cm^2 in consideration of the static system effect. The overall mass transfer coefficient of the isotope exchange reaction (2) on the surface of SiC is also quantified in consideration of the kinetic system effect by the numerical curve fitting method as 3.48×10^{-5} m/s. The value of the tritium trapping capacity or the mass transfer coefficient for SiC is smaller than that for metal and larger than that for graphite respectively. Quantifications of the tritium trapping capacity and the mass transfer coefficient make it possible to predict the behavior of tritium on the surface of SiC placed in water vapor atmosphere. The surface tritium decontamination for SiC by using the isotope exchange reaction (2) requires the longest operation time among three materials under high-temperature condition.

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