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Tritium permeation experiments using reduced activation ferritic/martensitic steel tube and erbium oxide coating

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Low concentration tritium permeation experiments have been performed on uncoated F82H and Er₂O₃-coated tubular samples in the framework of the Japan-US TITAN collaborative program. Tritium permeability of the uncoated sample with 1.2 ppm tritium showed one order of magnitude lower than that with 100% deuterium. The permeability of the sample with 40 ppm tritium was more than twice higher than that of 1.2 ppm, indicating a surface contribution at the lower tritium concentration. The Er₂O₃-coated sample showed two orders of magnitude lower permeability than the uncoated sample, and lower permeability than that of the coated plate sample with 100% deuterium. It was also indicated that the memory effect of ion chambers in the primary and secondary circuits was caused by absorption of tritiated water vapor that was generated by isotope exchange reactions between tritium and surface water on the coating.

Keywords: tritium, permeation, coating, erbium oxide, memory effect

1. Introduction

Understanding tritium migration behaviors in a fusion blanket is a key technology for the establishment of a fusion reactor fuel cycle. In a framework of the Tritium, Irradiation and Thermofluid for America and Nippon (TITAN) Japan-US collaborative program conducted in fiscal year 2007–2012, tritium permeation in fusion reactor materials including a tritium permeation barrier (TPB) has been investigated [1]. One of the remaining issues in tritium behaviors in the fusion materials is to clarify the permeation behavior at low partial pressure tritium for the interpolation to practical fusion blanket conditions. Regarding the TPB coatings, erbium oxide (Er₂O₃) thin films have recently shown remarkable permeation reduction factors using a physical vapor deposition method [2]. Moreover, Er₂O₃ coatings have been fabricated on plate substrates by not only spin-coating but also dip-coating process with a metal-organic decomposition (MOD) method [3,4]. However, the establishment of plant-scale fabrication of the coating, for example on a tubular substrate, is challenging. In this study, low concentration tritium permeation experiments have been carried out using reducing activation ferritic/martensitic (RAFM) steel tubular substrates and Er₂O₃ coatings fabricated by the liquid-phase method.

2. Experimental

2.1 Sample preparation

Electrolytically-polished RAFM steel F82H (8Cr-2W) tubes with dimensions of 150-mm length, 8-mm inner diameter, and 1.5-mm thickness were used as substrates. The MOD coating procedure is described in detail in the previous study [4]. First, the tube substrate was dipped into an Er₂O₃ coating precursor (Kojundo

Chemical Laboratory Co., Ltd. Er-03[®]) without addition of thinner, and then withdrawn at a constant speed of 1.2 mm s⁻¹ using a dip-coater. Second, the sample was placed in a dry oven set at 120 °C for 10 min to turn the solvent into a gel. Finally, the sample was heat treated in an infrared image furnace to decompose organic residues and to crystallize the Er₂O₃ coating. The heat-treatment condition was determined from the previous study [4]: at 700 °C for 10 min in hydrogen (purity: 99.9999%, O₂: < 0.02 ppm, H₂O: < 0.5 ppm) with approximately 0.6% moisture. The flow rate is less than 10 cm³ min⁻¹, and the rate of temperature increase and decrease is 100 and 30 °C min⁻¹, respectively. Moisture was added to the hydrogen flow by passing it through ice-chilled water. The coating process was repeated three times in order to increase coating thickness and reduce unevenness of the coating. The thickness of the coating was estimated as 0.3 μm on both inner and outer surfaces of the sample by the previous result [3]. Both ends of uncoated and coated samples were welded to prepare sample assemblies for the installation in a tritium permeation system which is describe in the next section.

2.2 Permeation setup

A conceptual diagram of the tritium permeation system is described in Fig. 1. The sample assembly was mounted in a quartz tube. Sample heating was conducted using an induction heater with a 1-turn, 5-inch-diameter coil made of copper. Tritium-helium mixture gas was introduced in a circuit (primary circuit) at a rate of 15 sccm (standard cm³ min⁻¹) and circulated at a rate of 1000 sccm using mass flow controllers to keep the tritium concentration in the circuit. Tritium that permeated outward through the sample was purged by a pure helium flow of 100 sccm in another circuit (secondary circuit). The tritium concentrations in the

primary and secondary circuits were examined with 10 and 1000 cm³ ion chambers which are called IC1 and IC2, respectively. After passing through the ion chambers, the circulating gas in the primary circuit was partly discharged at a rate of 15 sccm to a tritium recovery system placed in a ventilation hood, while the helium flow with purged tritium in the secondary circuit was once-through. In the ventilation hood, tritium concentrations of flowing gases from both circuits were again examined by the ion chambers: a 10 cm³ ion chamber is for the primary circuit (IC3) and a 1000 cm³ one for the secondary circuit (IC4).

The procedure of a gas-driven tritium permeation measurement is described as follows. After setting a test temperature using the induction heater, the system was conditioned for 2 h until the signals of ion chambers became stable. Then the pure helium flow in the primary circuit was switched to the tritium-helium mixture. The tritium concentration in the mixture gas cylinders was originally prepared as 3 and 65 ppm; however, it was actually measured as 1.2 and 40 ppm using ion chambers before and after a series of experiments. Since pressures in both circuits were set at 105 kPa, the tritium concentration of 1.2 and 40 ppm was corresponding to the partial pressure of 0.13 and 4.2 Pa. It took approximately 2 h to reach the steady state tritium concentration after introducing the tritium-helium mixture. The length of the work day limited the duration of the permeation experiments to less than 6 h.

One of the important issues in the evaluation of tritium permeation through tubular samples is how to determine a temperature distribution. The induction heating power was controlled by a thermocouple inserted in the center of the sample with its head touching the

inner wall. In this study, an infrared camera and a pyrometer were used to measure the temperature profile of the sample surface. The infrared camera could automatically store the temperature data only at more than 600 °C in two-dimensional display. On the other hand, the uncoated sample was measured by the pyrometer because lower test temperatures were required to avoid surface oxidation. The temperature profile at the permeation section was manually measured with vertically moving the position. The temperature distribution was calculated by Gaussian fitting to the surface temperature data.

The permeation phenomenon of hydrogen isotopes from the primary circuit which contains a known concentration to the secondary circuit with a negligible small concentration are represented by following equation [5]:

$$J = P \frac{P^{0.5}}{d}, \quad (1)$$

where J is the permeation flux, P is named permeability which is intrinsic parameter for the sample, p is the partial pressure of the hydrogen isotope introduced into the primary circuit, and d is the thickness of the sample. The pressure exponent represents permeation regime: the value of 0.5 indicates the rate-limiting process is diffusion of hydrogen isotope atoms, and the value of 1 means the rate-limiting process is dominated by molecular reactions such as adsorption and recombination at the sample surface. For a simple comparison with past results of deuterium permeation, Eq. (1) was applied for the calculation of tritium permeability in this study.

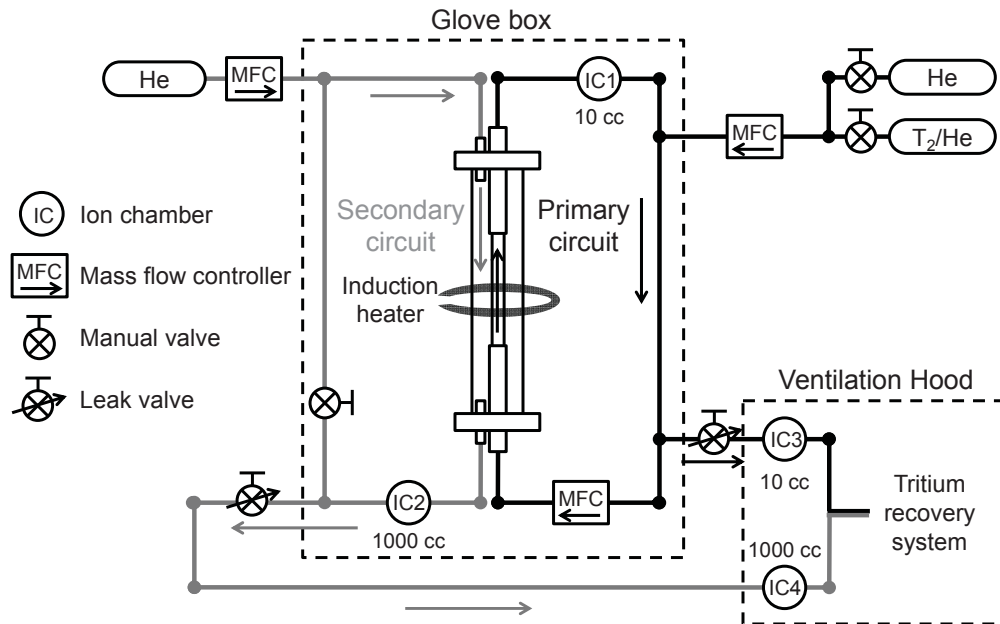


Fig. 1. Schematic view of the tritium permeation system.

3. Results and discussion

3.1 Uncoated sample

Figure 2 is a representative example of the tritium permeation experiments and illustrates temporal changes to the ion chamber concentrations with 40 ppm tritium in the primary and a temperature setting of 400 °C. Although the signal at the primary circuit reached steady state, the permeation flux to the secondary circuit continuously increased. Since the permeation flux that finally achieves equilibrium with the rate of discharge can be expressed by an exponential function, the permeation flux at the steady state was determined by fitting the secondary permeation flux.

Temperature dependence of tritium permeability is shown in Fig. 3. The uncoated sample tested with 1.2 ppm tritium at the setting temperature of 380–420 °C (average temperature: 361–393 °C) showed one order of magnitude lower permeability than that of the reference data with 100% deuterium [2]. In addition, the permeation measurements with 40 ppm tritium were more than twice larger than that with 1.2 ppm tritium. However, after the measurements at 400 and 420 °C with 40 ppm tritium, the permeability at 380 °C decreased to the level similar to the result with 1.2 ppm tritium probably due to the oxidation of the sample. A permeability comparable to the reference is supposed with higher tritium concentration, indicating a surface effect on the permeation at the low tritium concentration. The tendency of the permeation flux at a low partial pressure range (< 100 Pa) was also reported in deuterium permeation measurements [6]. The possible mechanism can be explained by the fraction of adsorption and recombination sites on the surface; the sites are saturated at the high partial pressure, while adsorption and recombination processes decrease the permeation rate at the low partial pressure range. Therefore, the tritium permeability similar to the reference with a high pressure hydrogen is expected with higher concentrations. However, it is notable that the tritium permeation rate at DEMO and commercial fusion reactor blankets might be overestimated when the permeability data obtained with the high pressure is applied.

3.2 Coated sample

The tritium permeation experiments on the Er_2O_3 -coated sample were performed at the setting temperature of 400–750 °C. However, no permeation signal was detected in a test duration at 600 °C or less because of a small permeation flux and a long diffusion time. Fig. 4 shows temporal changes of tritium driving pressure and permeation flux in the glove box (IC1 and IC2) and ventilation hood (IC3 and IC4) during the measurement with 1.2 ppm tritium at the setting temperature of 750 °C. The signals of IC1 and IC2 continuously increased at accelerated rates during the measurement, which was impossible especially in the primary circuit. This phenomenon had reproducibility in the measurements at 650 and 700 °C. On the contrary, the driving pressure in the ventilation hood (IC3) became stable, and the

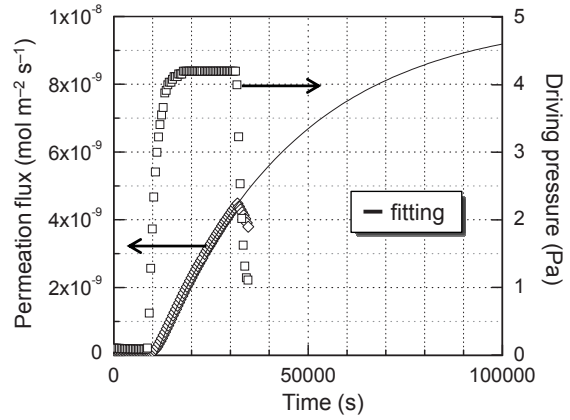


Fig. 2. Temporal changes and a fitting curve of tritium permeation flux and driving pressure on the permeation measurement of the uncoated F82H sample with 40 ppm tritium. The setting temperature was 400 °C, and the average temperature in the test section was 378 °C.

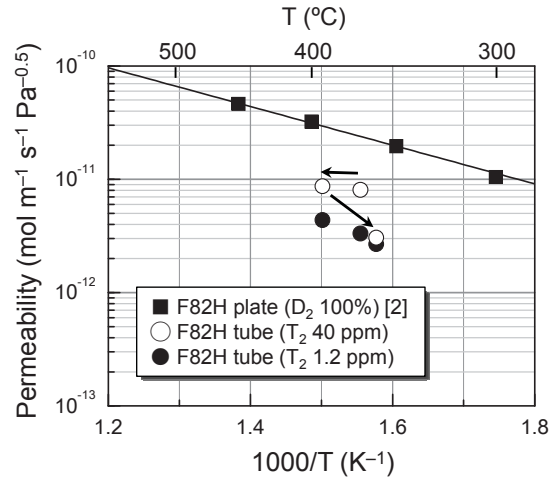


Fig. 3. Arrhenius plots of tritium permeability of the uncoated F82H samples. Deuterium permeability of the F82H plate sample is also presented [2].

permeation flux (IC4) showed a similar trend to Fig. 2.

It is reported that the memory effect of an ion chamber is mainly caused by the tritium transfer to surface water on electrodes in the ion chamber via adsorption or isotope exchange reactions [7]. Since the memory effect did not appear in the measurements on the uncoated sample as shown in Fig. 2, the surface water should exist on the Er_2O_3 coating in this case. Actually, a large amount of hydrogen due to surface water was detected on the surface of MOD coatings [8]. Therefore, the process of the memory effect can be explained as follows: (1) tritium adsorbed and permeated through the coated sample, (2) recombined and desorbed

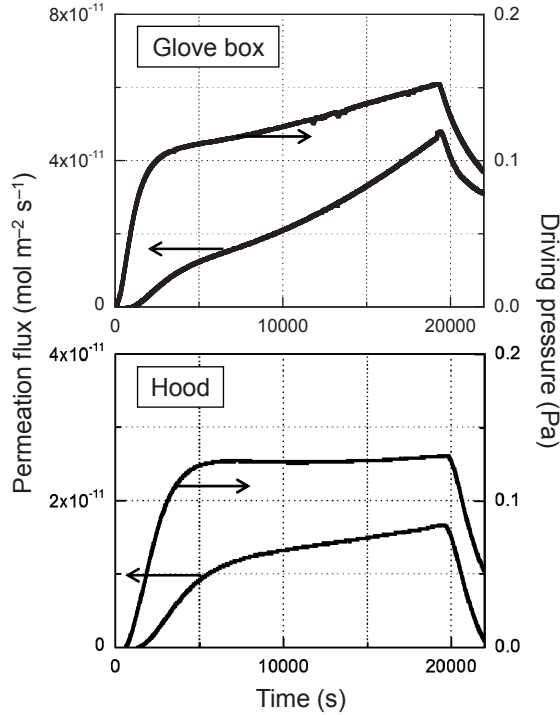


Fig. 4. Temporal changes of tritium permeation flux and driving pressure at the glove box and ventilation hood on the permeation measurement of the Er_2O_3 -coated F82H sample tested with 1.2 ppm tritium. The setting temperature was 750 °C, and the average temperature in the test section was 720 °C.

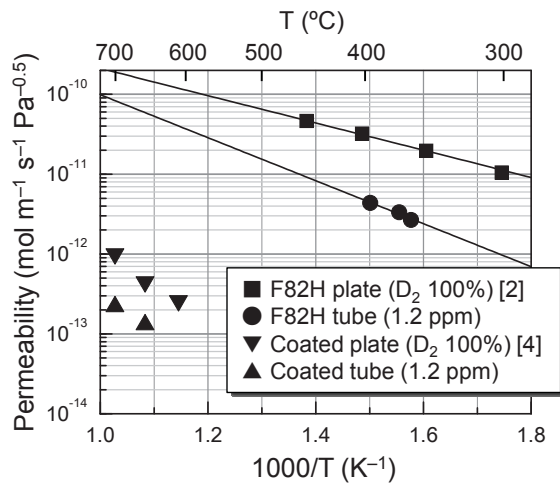


Fig. 5. Arrhenius plots of tritium permeability of the uncoated and Er_2O_3 -coated F82H tubular samples. Deuterium permeabilities of the uncoated and coated plate samples are also presented [2,4].

as HTO via isotope exchange reactions with H_2O on the surfaces of both inner and outer surfaces of the sample, (3) transferred by gas flows and adsorbed to the electrodes of IC1 and IC2. The ion chamber signals of IC3 and IC4 did not show a clear memory effect as shown in Fig. 4, although the longer time lags were observed due to the distance of approximately 5 m from the glove box. Therefore, the driving pressure and permeation flux of the coated sample were evaluated with the signals of IC3 and IC4. The tritium permeability of the uncoated and coated samples with reference data of deuterium permeability with plate samples are shown in Fig. 5 [2,4]. The coated tubular sample showed two orders of magnitude lower permeability than that of the uncoated one. Compared with the result of the coated plate sample tested with 100% deuterium, the permeability of the coated tubular sample tested with 1.2 ppm tritium also reduced to one-third or one-fourth, which is accorded with the trend in the results of the uncoated samples. Because several scratches were observed on the outer side of the coating after the welding process to prepare the sample assembly, the inner coating mainly contributed to the permeation reduction. Therefore, it is proved that the inner coating with a good uniformity and surface coverage has been achieved by the dip-coating process. In addition, the tritium permeability of the coating under the practical condition in a fusion reactor will be smaller than expected from the permeation data with high partial pressure hydrogen isotopes due to the contribution of the surface effect.

4. Summary

Gas-driven permeation experiments with low concentration tritium have been performed on uncoated and Er_2O_3 coated F82H tubular samples. The uncoated sample tested with 1.2 ppm tritium showed one order of magnitude lower permeability than that of a plate sample with 100% deuterium. The permeability of the sample with 40 ppm was more than twice higher than that of 1.2 ppm, indicating a surface effect at the low tritium concentration. The Er_2O_3 -coated sample with 1.2 ppm tritium showed two orders of magnitude lower permeability than the uncoated sample, and less permeability than that of the coated plate sample with 100% deuterium. It was found that the memory effect of ion chambers in both circuits was caused by tritiated water vapor which was generated by isotope reactions between tritium and surface water on the coating and transferred to the electrodes of the ion chambers. An Er_2O_3 coating on the tubular sample with a good uniformity and surface coverage has been achieved by the dip-coating process.

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