

**Deuterium Permeation Behavior of Erbium Oxide Coating  
on Austenitic, Ferritic, and Ferritic/Martensitic Steels**

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**Abstract**

Tritium permeation barrier is required in fusion blanket for reduction of loss of fuel and health hazard. In this study, deuterium permeation experiments have been

performed on four kinds of steels and erbium oxide coatings fabricated by a filtered arc deposition method. The permeation flux of uncoated samples shows diffusion-limited regime in the temperature range 573–723 K and the permeability is corresponding to literature data. The coated samples deposited at room temperature have been tested at 773 K. It is found that the coatings suppress the deuterium permeation to a close level in spite of different types of steel substrates. In addition, the exponent of the driving pressure slightly changes compared to the uncoated sample. However, the permeation regime is still near diffusion limited.

**Keywords:** Hydrogen, Tritium permeation barrier, Coating, Erbium oxide

## **1. Introduction**

One of the most important requirements in fusion power plant is a safe operation of radioactive tritium. Since structural materials such as steels generally have high permeability of hydrogen isotopes in the operational temperature range, suppression of tritium permeation through wall of duct is a key investigation. Thin ceramic coatings on steel substrates have been tested for many years and shown reduction of hydrogen isotope permeability [1–12]. Aluminum oxide (alumina,  $\text{Al}_2\text{O}_3$ ) is a major candidate for

the research today because of high permeation reduction factor (PRF), good thermal property, and so on. However, the difficulty exists in formation of  $\alpha$ -alumina phase which needs high temperature.

Recently erbium oxide (erbia,  $\text{Er}_2\text{O}_3$ ) is also thought to be a candidate for TPB material because it has high stability under strong reducing atmosphere as well as capability to suppress hydrogen isotope permeation [13]. The  $\text{Er}_2\text{O}_3$  coating has been investigated as insulator for liquid lithium blanket system [14, 15]. Therefore there are limited data as TPB and the permeation mechanism through the coating has not been clarified yet.

In the present study, the deuterium permeation measurements were performed by means of a gas-phase deuterium permeation apparatus, and the deuterium permeation properties of four kinds of steels and the  $\text{Er}_2\text{O}_3$  coatings deposited by a PVD technique were reported.

## **2. Experimental**

### 2.1. Deposition of $\text{Er}_2\text{O}_3$ coating

Four kinds of steels are used in this study as substrates: austenitic SS316 (Fe-18Cr-12Ni-2.5Mo), ferritic SS430 (Fe-18Cr), reduced activation ferritic/martensitic

(RAFM) steels JLF-1 (Fe-9Cr-2W) and F82H (Fe-8Cr-2W, Heat No. 9753 42W-4). Samples are disks of 20 mm in diameter or squares of 25 mm on a side, 0.5 mm in thickness, and both sides are mirror polished. About 1  $\mu\text{m}$   $\text{Er}_2\text{O}_3$  film is deposited by a filtered arc deposition device described in [13] and [16]. A schematic view of the device is shown in Fig. 1. An arc discharge on an erbium cathode (99.9% Er) with filtering plasma from metal droplets and introducing oxygen into the main chamber forms the erbium oxide film. The coating is deposited on the substrate at room temperature with applying RF-induced bias voltages of  $-150$  V to enhance crystallinity. The reason why the coating has been deposited at room temperature is to avoid peel-off of the coating after deposition because of the difference of thermal expansion coefficient between the coating and the substrate.

## 2.2. Permeation measurement

The permeation apparatus shown in Fig. 2 is assembled on a basis of a principle described in [17]. A sample is sealed with two nickel C-rings with inconel coil spring inside (U-TIGHT SEAL®) and can be heated up to 973 K by electric furnace.

Two parts of the apparatus divided by the sample are separately evacuated up to about  $10^{-6}$  Pa, and then deuterium (purity of 99.995%) is introduced into one side

(called upstream) at  $10^4$ – $10^5$  Pa. The pressure of the upstream is measured by two gauges: a cold-cathode/pirani gauge (Canon ANELVA Technix M-360CP-SP) for the range of  $10^{-7}$ – $10^{-2}$  Pa and a capacitance gauge (Canon ANELVA Technix M-340DG-13) for  $10^2$ – $10^5$  Pa. Measuring partial pressure of deuterium permeating through the sample to another side (called downstream) is performed by quadrupole mass spectrometer (QMS, Canon ANELVA Technix M-201QA-TDM). A cold-cathode/pirani gauge is also installed at the downstream for checking vacuum and QMS calibration. The downstream is continuously pumped during the experiments and the QMS works within the range of  $10^{-9}$ – $10^{-5}$  mol/m<sup>2</sup>s for D<sub>2</sub> in this system.

The process of the permeation measurements is as follows. The coated sample is mounted with the coating facing the upstream because contamination molecules are expected to exist in the upstream at high pressures and uncoated side of the sample would be oxidized in such atmosphere during the measurements. The coated samples are heated up to 873 K before setting a test temperature to release remaining gases such as H<sub>2</sub> and CO<sub>2</sub> for better vacuum condition. However, the uncoated samples are not heated for avoiding oxidation of the surface. After the test temperature has become stable, the deuterium gas is introduced from variable leak valve in sequence:  $1.00 \times 10^4$ ,

$2.00 \times 10^4$ ,  $4.00 \times 10^4$  and  $8.00 \times 10^4$  Pa, for example. When a permeation rate at the downstream has reached steady state, the deuterium is added up to the next pressure.

Permeation phenomena of hydrogen are represented by following equation [18]:

$$J = P p^n / d$$

where  $J$  is the permeation flux,  $P$  is named permeability which is intrinsic parameter for the sample,  $p$  is the driving pressure introduced into the upstream, and  $d$  is the thickness of a sample. The exponent  $n$  represents permeation regime: diffusion limited and surface limited when  $n = 0.5$  and 1, respectively.

### 3. Results and discussion

#### 3.1. Bare samples

Fig. 3 demonstrates an example of the permeation flux  $J$  dependence on the driving pressure  $p$  with the JLF-1 sample. Double logarithmic plots of the data are linearly-related. Furthermore, the exponent  $n$  showed 0.51–0.53 at 573–723 K which indicates the deuterium passed through the sample according to diffusion limited. The  $n$  value of 0.56 at 773 K and 0.62 at 873 K indicates oxidation of the surface. The  $n$  value of ferritic and ferritic/martensitic SS430, JLF-1 and F82H increased at more than 773 K, on the contrary, the austenitic SS316 sample showed 0.51–0.54 in the temperature range

of 573–873 K which means the austenitic steel was relatively less oxidized at more than 773 K. In order to examine chemical composition of the surface of the sample, depth profiles of the JLF-1 sample before and after permeation measurements were obtained by means of X-ray photoelectron spectroscopy (XPS). The Fe/O ratio shows about 4 before the measurements and 1 after the measurements, which indicates surface oxidation

The temperature dependence on the permeability  $P$  through the steel samples is shown in Fig. 4. The data of F82H from literature is also given [19]. The data on the permeability of the steels are spread by about 1 order of magnitude. This is thought to be because of different chemical compositions and crystal structures. On the other hand, the RAFM steel JLF-1 and F82H have similar values on the permeability.

In previous study [20], the permeability of the JLF-1 sample was reported 1–2 orders of magnitude lower than that of a kind of RAFM steels, EUROFER'97 (Fe-9Cr-1W) which had been obtained a close value of permeability to F82H. It is proved in the present study that the JLF-1 steel also has similar permeability to the other RAFM steels such as F82H and EUROFER'97. However it has been oxidized at more than 773 K.



### 3.2. Coated sample

Fig. 5 shows the comparison of the permeation flux  $J$  between the bare and coated samples at 773 K. First, the permeation flux of the coated sample was 2–3 orders of magnitude less than that of the substrate. It is found that the  $\text{Er}_2\text{O}_3$  coatings show efficient suppression of the deuterium permeation when deposited at room temperature. Second, the flux of the bare samples is different about 1 order of magnitude among materials. However, the coated samples on the different types of steel decreased the permeation flux to a close level. Although scattered PRF values (40–700) naturally derive from the difference of permeability of the bare samples, it is believed the quality of the coatings on different types of steels is same.

The exponent  $n$  of the coated samples are also given in Fig. 5. Though a slight change is seen on each coating, the values (0.44–0.62) are still around 0.5. This result indicates that the deuterium passed through the coating according to diffusion-limited regime and surface effects such as absorption is small.

## 4. Summary

Deuterium permeation measurements on four kinds of steels and the  $\text{Er}_2\text{O}_3$  coatings deposited by a PVD method have been performed. Diffusion-limited regime

was confirmed on the bare samples at 573–723 K and the permeability of the SS316 and F82H bare samples showed correspondence to the literature. It is found that the JLF-1 sample has similar permeability as F82H and has been oxidized at more than 773 K. The coated samples deposited at room temperature decreased deuterium permeation to the close level in spite of different permeability of the substrates. The exponent  $n$  indicates that the deuterium permeation through the coated sample follows diffusion-limited regime and surface effects by the coating is small.

## **5. Acknowledgement**

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Figure and figure captions

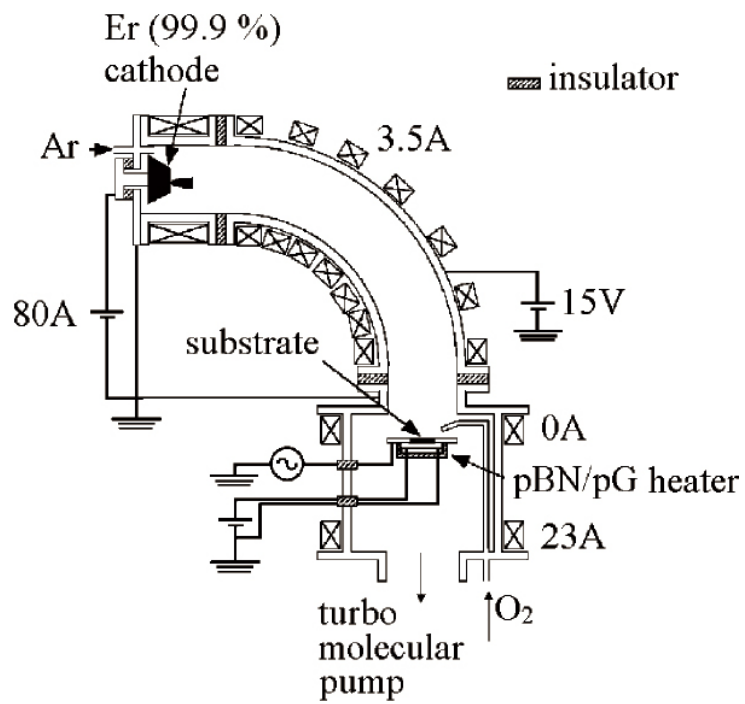


Fig. 1. Schematic view of the filtered arc deposition device.

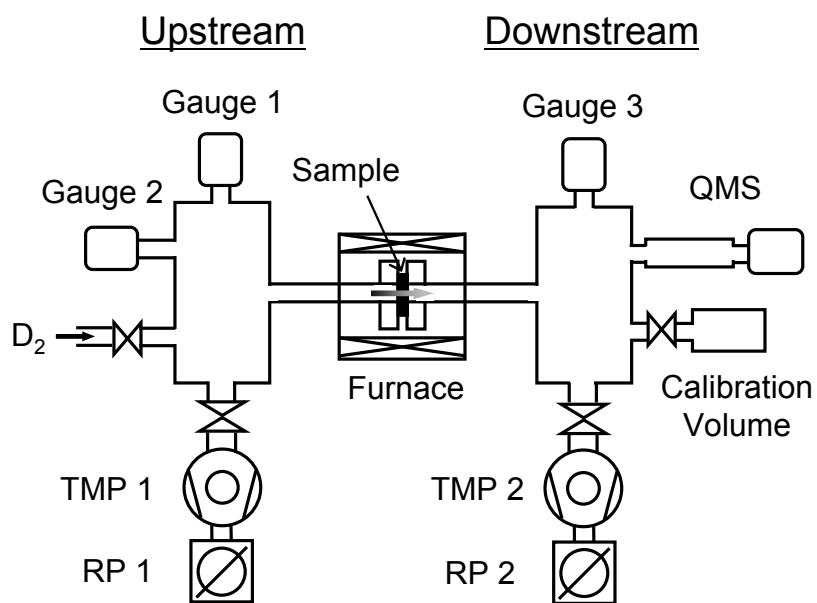


Fig. 2. Schematic view of the hydrogen permeation apparatus.

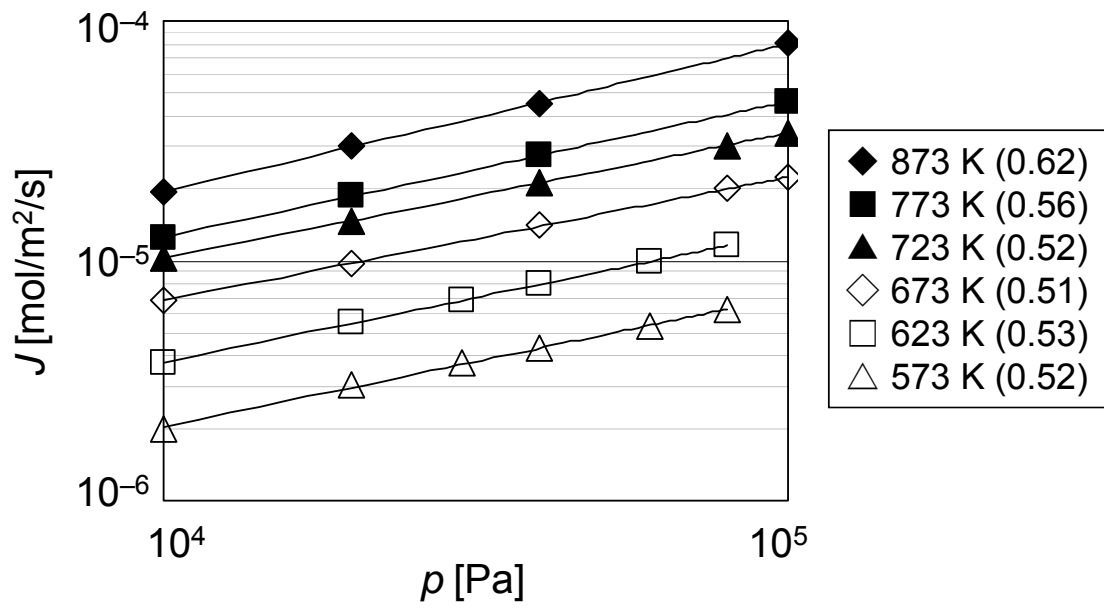


Fig. 3. Deuterium permeation flux through JLF-1 as a function of the driving pressure at different temperatures. Numbers in parenthesis represent the pressure exponent  $n$ .

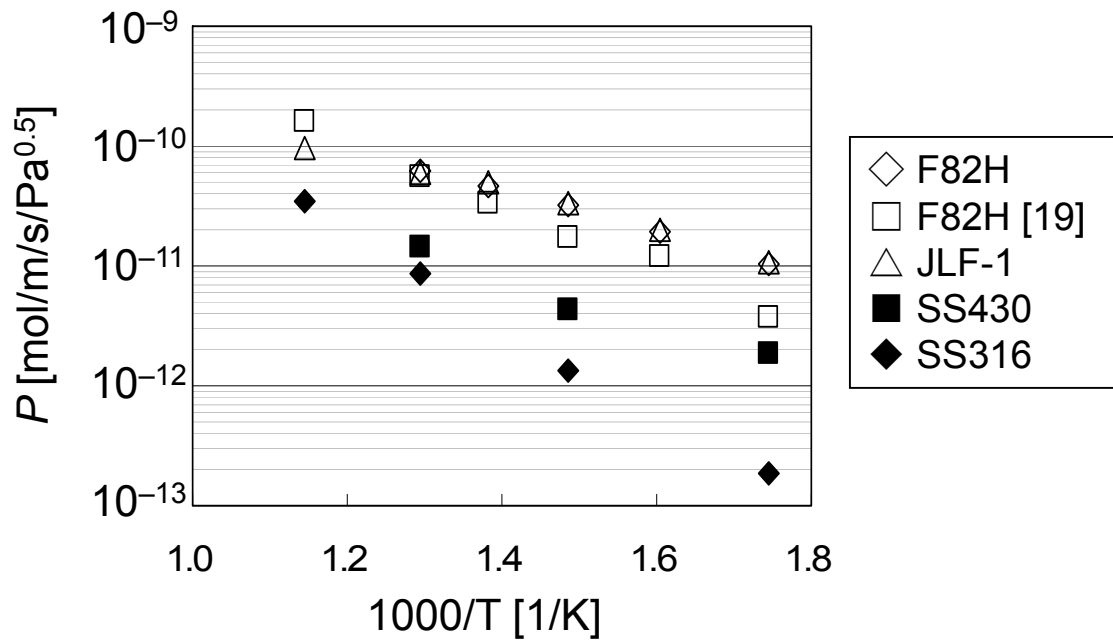


Fig. 4. An Arrhenius plot of deuterium permeability of the bare steel samples. A F82H data is also given from [19].



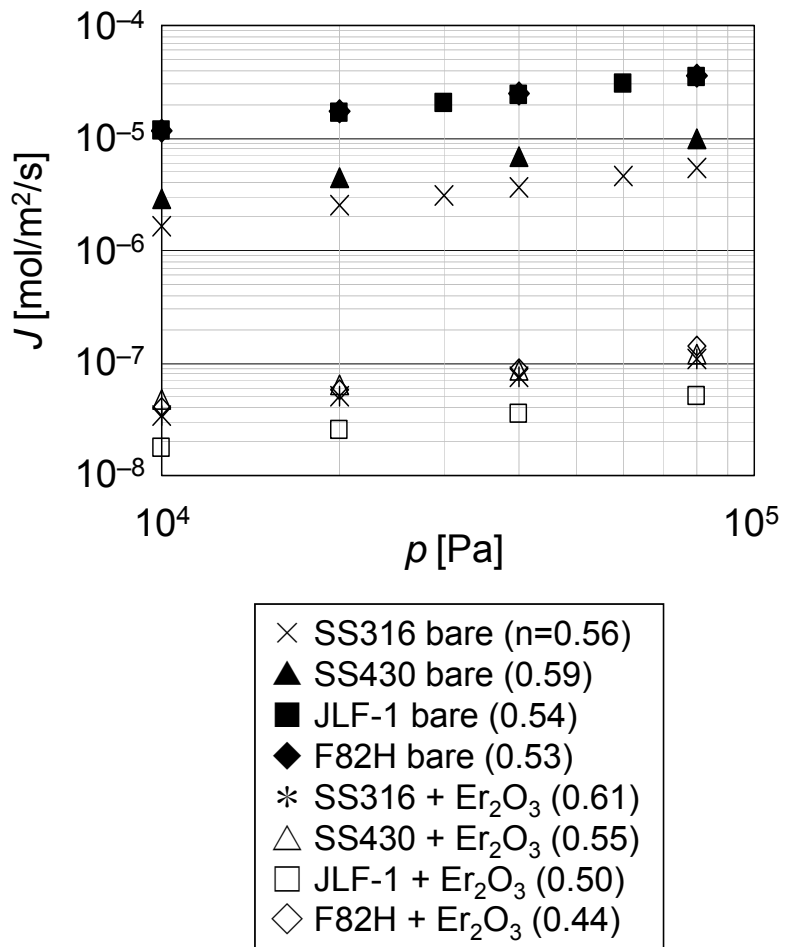


Fig. 5. Comparison of deuterium permeation flux on the bare samples and the coatings deposited at room temperature as a function of the driving pressure. The test temperature is 773 K. Numbers in parenthesis represent the pressure exponent  $n$ .