

## Deuterium Permeation Mechanism in Erbium Oxide Coatings for Tritium Permeation Barrier

T. Chikada<sup>1</sup>, A. Suzuki<sup>1</sup>, T. Tanaka<sup>2</sup>, T. Kobayashi<sup>3</sup>, H. Maier<sup>4</sup>, T. Terai<sup>1</sup>, and T. Muroga<sup>2</sup>

<sup>1</sup> *School of Engineering, University of Tokyo, Tokyo 113-8656, Japan*

<sup>2</sup> *National Institute for Fusion Science, Gifu 509-5292, Japan*

<sup>3</sup> *Institute of Physical and Chemical Research (RIKEN), Saitama 351-0198, Japan*

<sup>4</sup> *Max-Planck-Institut für Plasmaphysik, D-85748 Garching, Germany*

Development of tritium permeation barrier is considered one of principal investigations to build up a fuel cycle in a fusion power plant. For the practical application as tritium permeation barrier, fabrication of erbium oxide coatings by metal-organic decomposition method has been carried out on reduced activation ferritic/martensitic steels. The coated samples showed various surface states after the heat-treatment process under different conditions. An oxide layer was generated between the erbium oxide coating and the substrate when heat-treated in high purity argon. It is indicated that the oxide layer has caused defects in the coating and resulted in the degradation of the samples during deuterium permeation measurements. The sample heat-treated in high purity hydrogen with moisture shows the thinner oxide layer and stable permeation fluxes during the measurements. A coating of 0.3  $\mu\text{m}$  in thickness indicates a permeation reduction factor of 700–1000 at 773–973 K, which is a comparable level to the coating deposited by physical vapor deposition technique performed in the previous study.

**Keywords:** tritium, hydrogen, permeation barrier, ceramic coating, erbium oxide

### I. Introduction

Over the past few decades, investigations on a control of tritium have been pursued for the realization of prototype reactors (DEMO) and commercial fusion power plants. The development of suppressing tritium permeation through wall of ducts in a blanket system is one of the essential tasks since structure materials such as reduced activation ferritic/martensitic (RAFMs) steels have high permeability of hydrogen isotopes in the operational temperature range. Fabrication of thin ceramic coatings is a promising solution for reducing tritium loss, and thereby tritium permeation barrier (TPB) coatings have been studied for many years

[1–7].

Recently erbium oxide (erbia,  $\text{Er}_2\text{O}_3$ ) coatings have been investigated as insulating coatings for self-cooled lithium blankets [8,9]. It was clarified that the  $\text{Er}_2\text{O}_3$  coatings suppressed deuterium permeation to a level similar to Al-based coatings which have been investigated chiefly in history [10, 11]. However, the previous studies on the  $\text{Er}_2\text{O}_3$  coating have employed a physical vapor deposition (PVD) which is not suitable for a plant-scale fabrication.

In our previous work [12], the metal-organic decomposition (MOD) method, which is capable to fabricate oxide coatings on tubes or other complex shape substrates by

coating with the erbium metal solvent, was demonstrated to form the  $\text{Er}_2\text{O}_3$  coating for the first time on a SS316 plate substrate. However, compositions and microstructures of substrate materials are expected to affect coating properties during the fabrication process. Moreover, the microstructure analysis of the coating is needed to understand a formation mechanism of the  $\text{Er}_2\text{O}_3$  as well as a permeation behavior of hydrogen isotopes. Consequently, in this paper, the  $\text{Er}_2\text{O}_3$  coatings have been fabricated on RAFM steels by MOD method, and then analyses and deuterium permeation measurements of the coating have been performed to evaluate the microstructure of the coating and its properties as a TPB.

## II. Experimental

### II. A. Sample Preparation

The MOD method is quite similar to the sol-gel method in coating procedure: 1) coating a liquid precursor on a substrate by spin-coating or dip-coating, 2) drying for solidification, and then 3) heat-treating to crystallize the coating as an erbium oxide. In the present work, the spin-coating technique was employed to fabricate uniform coatings on plate substrates.

The RAFM steels F82H (8Cr-2W, Heat No. 9753 42W-4) and JLF-1 (9Cr-2W) are used as substrates. Square-shaped plates of 25 mm on a side and 0.5 mm in thickness are mirror polished. Firstly, the erbium organic solvent (Kojundo Chemical Laboratory Co., Ltd. Er-03<sup>®</sup>) which contains 2.7–3.3 wt% erbium carboxylic acid is put on the substrate and homogenized by a spin-coater. The spin-coater was operated at the rate of 500 rpm for 10 s and then 2000 rpm for 20 s to remove superfluous droplets and spread the solvent to the substrate. This drop and rotating process is repeated for 5 times to obtain a flat surface. Secondly, the sample is put on a hot plate set at 393 K for 10 min to dry the

solvent. In this process, the solvent turns to a gel. Finally, to crystallize the  $\text{Er}_2\text{O}_3$  coating, the sample is heat-treated at 873–973 K for 10–30 min in argon (purity of 99.9999%,  $\text{O}_2 < 0.05$  ppm,  $\text{H}_2\text{O} < 0.5$  ppm) or hydrogen (purity of 99.9999%,  $\text{O}_2 < 0.02$  ppm,  $\text{H}_2\text{O} < 0.5$  ppm) with about 0.6% moisture by infrared image furnace. The flow rate is 10–20 ml/min and the rate of temperature increase and decrease is 20–30 K/min. The moisture is added in the hydrogen by passing through ice chilled water in order to control the moisture concentration in the atmosphere by known saturated vapor pressures.

### II. B. Analysis

As for the analysis of the coating, the surface of the coating is examined using a laser microscope. The crystal structure of the coating is analyzed using X-ray diffraction (XRD). The cross-section of the coating is examined using field emission scanning electron microscopy (FE-SEM). The composition-reflected images are achieved with this equipment by detecting backscattering electrons. The chemical analysis using energy dispersive X-ray spectroscopy (EDX) is also available.

The deuterium permeation equipment and the experimental procedure are described in detail in [11]. To briefly explain the scheme, 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%) of  $10^4$ – $10^5$  Pa is introduced into one side (called upstream) with a leak valve. The sample is mounted with the coating facing the upstream for avoiding surface oxidation on uncoated side of the sample by contamination molecules. A flux of deuterium permeation through the sample to another part (called downstream) is measured by quadrupole mass spectrometer (QMS). The downstream chamber is continuously pumped during the experiments and the QMS works within the range of  $10^{-10}$ – $10^{-5}$  mol/m<sup>2</sup>s for  $\text{D}_2$  in this

method with secondary electron multiplier. When the permeation flux at the downstream has reached steady state, the deuterium is added up to the next pressure. The temperature of the sample during measurements is set at 773–973 K to increase the permeation rate to a detectable level.

When diffusion limits gas permeation through a sample rather than surface reactions, the permeation flux is typically represented by following equation [13]:

$$J = P p^{0.5} / d$$

where  $J$  is the permeation flux ( $\text{mol m}^{-2} \text{s}^{-1}$ ),  $P$  is named permeability ( $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-0.5}$ ) which is intrinsic parameter for the sample,  $p$  is the driving pressure (Pa), and  $d$  is the thickness of the sample (m).

### III. Results and Discussion

#### III. A. Heat-treatment in Ar

The surface observation was performed for four samples heat-treated under different conditions. The sample (a), which has been heat-treated at 873 K for 60 min with the rate of temperature increase and decrease of  $20 \text{ K min}^{-1}$ , shows a rough surface of the coating on F82H substrate. When heat-treated at 973 K for 30 min as the sample (b), the coating also shows a rough surface and some holes. Meanwhile the sample (c) and (d) show relatively smooth surfaces when treated at 973 K for 10–20 min with the rate of temperature increase and decrease of  $30 \text{ K min}^{-1}$ .

XRD patterns of the coatings are indicated in Fig. 1. The peak at  $29.4^\circ$  deriving from  $\text{Er}_2\text{O}_3$  (222) are seen in every sample. However, the peak is broad and the diffraction intensity is quite low, which means the coatings have not been crystallized sufficiently. In addition, the peaks representing  $(\text{Fe, Cr})_2\text{O}_3$  are seen in the sample (a) and (b) at around  $24^\circ$ ,  $33^\circ$ , and  $35.5^\circ$ , while they are weak in the sample (c) and (d).

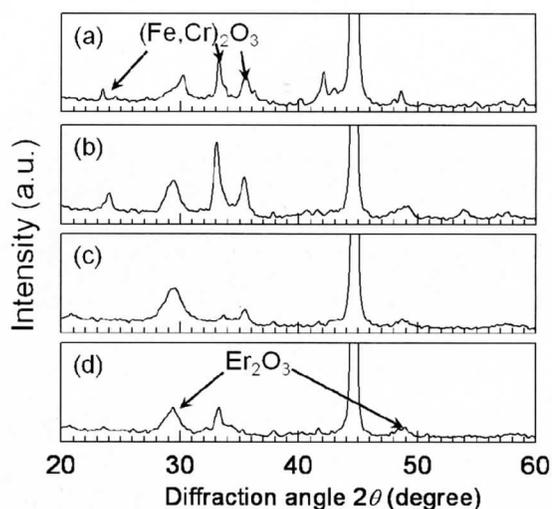


Fig. 1. XRD spectra of the samples heat-treated in high purity argon under various conditions: (a) heat-treated at 873 K for 60 min, (b) at 973 K for 30 min, (c) at 973 K for 20 min, and (d) at 973 K for 10 min. The rates of temperature increase and decrease was  $20 \text{ K min}^{-1}$  for sample (a) and (b),  $30 \text{ K min}^{-1}$  for sample (c) and (d), respectively.

Therefore, it is proved that the rough surface has been resulted from the  $(\text{Fe, Cr})_2\text{O}_3$  phase.

Figure 2 illustrates the cross-section image of the sample (a) by FE-SEM. It is clearly seen that the coating has formed a four-layer structure which has consisted in sequence of the F82H substrate, the Fe-Cr-O layer, the dense  $\text{Er}_2\text{O}_3$ , and the uncrystallized region. The substantial thickness of the  $\text{Er}_2\text{O}_3$  coating is found to be  $0.2\text{--}0.3 \mu\text{m}$ . Besides, gaps are seen in the Fe-Cr-O layer. In the reference [14], it is suggested that the oxide layer of JLF-1 substrate has caused peeling of the  $\text{Er}_2\text{O}_3$  coating deposited at 973 K by a PVD method. In the same way, it is expected that the gaps in the oxide layer have caused the rough surface of the coating. Deuterium permeabilities of the uncoated F82H substrate, the sample (a), (b), and (c) as a function of the inverse of the test temperature are shown in Fig. 3. As for the sample (a) and (b), values of permeation reduction factor (PRF) which is obtained by

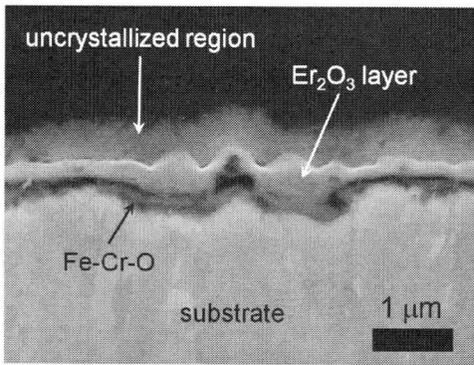


Fig. 2. A cross-section FE-SEM image of the sample (a).

dividing the permeability of the bare sample by that of the coated one are less than 5 at 773 and 873 K. The result suggests that the rough surface of the coating has caused generation of holes or cracks reaching the substrate, and thus deuterium has passed through the defects as shortcut. On the other hand, the sample (c) has shown a PRF value of 200 in the first measurement at 873 K. However, the permeation suppression efficiency has degraded to a PRF of 30 as the measurements have run. It is expected that the crystallized coating has damaged during temperature change because of the inhomogeneous oxide layer. In addition, the permeability of the sample (d) which is not

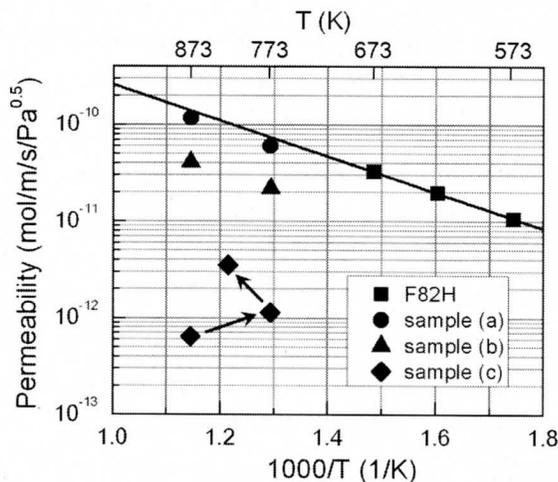


Fig. 3. Arrhenius plots of deuterium permeability of the bare F82H and the coated samples heat-treated in high purity argon.

shown in Fig. 3 has indicated similar outcome to the sample (c). In our previous work [12], the optimized heat treatment condition for the coating on the 316 stainless steel substrate was at 973 K for 60 min with the rate of temperature increase and decrease of 20 K/min in high purity argon. By comparing the results, it is found that the RAFM substrates are liable to be oxidized more strongly than the 316 stainless steel during the heat treatment. Therefore, a quicker and more moderate heat-treatment condition is necessary to fulfill crystallization of the  $\text{Er}_2\text{O}_3$  with avoiding strong oxidation of the RAFM substrates.

### III. B. Heat-treatment in $\text{H}_2$ with $\text{H}_2\text{O}$

To reduce the oxide layer of the substrate, the heat treatment in high purity hydrogen with about 0.6% moisture has been performed. The samples were heat-treated at 973 K for 10 min with the rate of temperature increase and decrease of  $30 \text{ K min}^{-1}$ . The sample (f) was coated 3 times using the same process. Both coatings are uniform and no micron-size holes and cracks are seen from the surface observation using SEM.

XRD spectra of the samples are illustrated in Fig. 4. The peaks of  $(\text{Fe, Cr})_2\text{O}_3$  are not clearly seen in the sample (e), though the peaks of  $\text{Er}_2\text{O}_3$  is weak. On the other hand, the sharp peak at  $29.4^\circ$  deriving from  $\text{Er}_2\text{O}_3$  (222) is seen in the sample (f). In addition, other peaks of  $\text{Er}_2\text{O}_3$  (400) (440), and (622) are also seen at  $34$ ,  $49$ , and  $58^\circ$ , respectively. It is indicated that the heat treatment in high purity hydrogen with moisture is an effective atmosphere to avoid formation of the  $(\text{Fe, Cr})_2\text{O}_3$  layer and crystallize the  $\text{Er}_2\text{O}_3$  coating. Moreover, thicker coatings can be produced by repeating the coating procedure.

The cross-section image of the sample (f) is shown in Fig. 5. In this case, the thickness of the

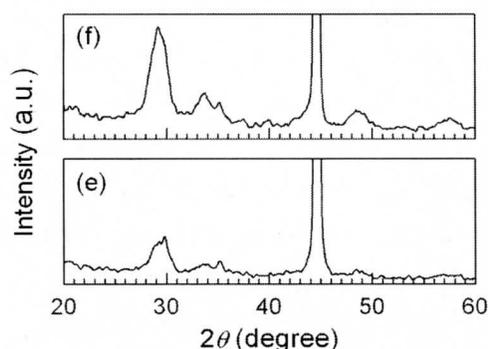


Fig. 4. XRD patterns of the samples heat-treated at 973 K in high purity hydrogen with moisture. The sample (e) and (f) were coated once and 3 times, respectively.

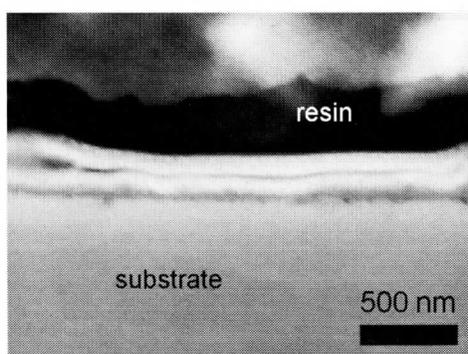


Fig. 5. A cross-section FE-SEM image of the sample (f) shown in Fig. 4. The layer structure of the coating is derived from the repeated coating processes.

Fe-Cr-O layer is estimated approximately 50 nm, which is much thinner than that in Fig. 2. It is proved that the thick Fe-Cr-O layer has caused the rough surface of the coating and can be avoided by the heat treatment in high purity hydrogen with moisture.

Figure 6 shows deuterium permeabilities of the samples at 773–973 K. The measurements have been repeated more than twice at each temperature to confirm reproducibility of the data with the variation of less than 10%. Both samples have shown stable permeabilities and no degradation have been seen. From the viewpoint of PRF, values of 100 at the sample (e) and 500–700 at the sample (f) were

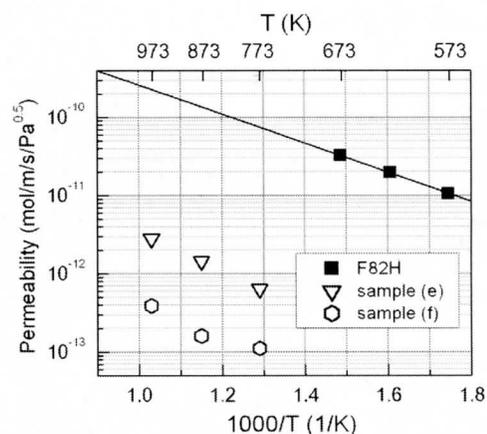


Fig. 6. Arrhenius plots of deuterium permeability of the bare F82H and the samples heat-treated in hydrogen with 0.6% moisture.

estimated. That means the thickness of the coating can be increased by repeating the coating procedure. Furthermore, the 0.3  $\mu\text{m}$ -thick coating as shown a comparable reduction efficiency to the 1  $\mu\text{m}$ -thick one fabricated by physical vapor deposition. Therefore, the MOD coating is promising for the practical application as TPB.

#### IV. Summary

The  $\text{Er}_2\text{O}_3$  coating has been fabricated on the RAFM steels by the MOD method. The samples heat-treated in high purity argon indicate the rough surface generated by the Fe-Cr-O layer and degradation during deuterium permeation measurements at 773–873 K. The uniform surface with high sufficiency of deuterium permeation has achieved by the heat-treatment in high purity hydrogen with moisture. The coating of 0.3  $\mu\text{m}$  in thickness has shown reduction factors of 500–700 and data reproducibility at 773–973 K, which is comparable efficiency to 1  $\mu\text{m}$ -thick coatings fabricated by physical vapor deposition. Additionally, it is expected that higher PRFs can be obtained by repeating the coating process on the request of blanket systems.

## Acknowledgements

This work was supported in part by KAKENHI (19055001), Ministry of Education, Culture, Sports, Science and Technology, Japan and Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

## References

- [1] G.W. Hollenberg, E.P. Simonen, G. Kalinin, A. Terlain, "Tritium/hydrogen barrier development," *Fusion Eng. Design*, **28**, 190–208 (1995).
- [2] A. Perujo, K.S. Forcey, "Tritium permeation barriers for fusion technology," *Fusion Eng. Design*, **28**, 252–257 (1995).
- [3] G. Benamati, C. Chabrol, A. Perujo, E. Rigal, H. Glasbrenner, "Development of tritium permeation barriers on Al base in Europe," *J. Nucl. Mater.*, **271&272**, 391–395 (1999).
- [4] A.J. Magielsen, K. Bakker, C. Chabrol, R. Conrad, J.G. van der Laan, E. Rigal, M.P. Stijkel, "In-pile performance of a double-walled tube and a tritium permeation barrier," *J. Nucl. Mater.*, **307–311**, 832–836 (2002).
- [5] A. Aiello, I. Ricapito, G. Benamati, A. Ciampichetti, "Qualification of tritium permeation barriers in liquid Pb-17Li," *Fusion Eng. Design*, **69**, 245–252 (2003).
- [6] J. Konys, A. Aiello, G. Benamati, and L. Giancarli, "Status of tritium permeation barrier development in the EU," *Fusion Sci. Technol.*, **47**, 844–850 (2005).
- [7] M. Nakamichi, T.V. Kulsartov, K. Hayashi, S.E. Afanasyev, V.P. Shestakov, Y.V. Chikhray, E.A. Kenzhin, A.N. Kolbaenkov, "In-pile tritium permeation through F82H steel with and without a ceramic coating of Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> including CrPO<sub>4</sub>," *Fusion Eng. Design*, **82**, 2246–2251 (2007).
- [8] B. A. Pint, P.F. Tortorelli, A. Jankowski, J. Hayes, T. Muroga, A. Suzuki, O.I. Yeliseyeva, V.M. Chernov, "Recent progress in the development of electrically insulating coatings for a liquid lithium blanket," *J. Nucl. Mater.*, **329–333**, 119–124 (2004).
- [9] T. Muroga, J.M. Chen, V.M. Chernov, K. Fukumoto, D.T. Hoelzer, R.J. Kurtz, T. Nagasaka, B.A. Pint, M. Satou, A. Suzuki, H. Watanabe, "Review of advances in development of vanadium alloys and MHD insulator coatings," *J. Nucl. Mater.*, **367–370**, 780–787 (2007).
- [10] D. Levchuk, S. Levchuk, H. Maier, H Bolt, A. Suzuki, "Erbium oxide as a new promising tritium permeation barrier," *J. Nucl. Mater.*, **367–370**, 1033–1037 (2007).
- [11] T. Chikada, A. Suzuki, Z. Yao, D. Levchuk, H. Maier, T. Terai, T. Muroga, "Deuterium permeation behavior of erbium oxide coating on austenitic, ferritic, and ferritic/martensitic steels," *Fusion Eng. Design*, **84** (2009) 590–592.
- [12] Z. Yao, A. Suzuki, D. Levchuk, T. Chikada, T. Tanaka, T. Muroga, T. Terai, "Hydrogen permeation through steel coated with erbium oxide by sol-gel method," *J. Nucl. Mater.*, **386–388**, 700–702 (2009).
- [13] K.S. Forcey, D.K. Ross, J.C.B. Simpson, D.S. Evans, "Hydrogen transport and solubility in 316L and 1.4914 steels for fusion reactor application," *J. Nucl. Mater.*, **160**, 117–124 (1988).
- [14] T. Chikada, A. Suzuki, T. Kobayashi, Z. Yao, D. Levchuk, H. Maier, T. Terai, T. Muroga, "Thermal Influence on Erbium Oxide Coating for Tritium Permeation Barrier," *Fusion Sci. Technol.*, **56**, 309–313 (2009).