Deuterium Permeation in an Er$_2$O$_3$ Thin Film Fabricated on a Type-316L Stainless-Steel Substrate

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A metal-oxide film can be used as a hydrogen-isotope permeation barrier in a fuel circulation system for nuclear fusion. We fabricated an Er$_2$O$_3$ thin film on a type-316L stainless-steel substrate by using a metal-organic chemical vapor deposition technique for use as a hydrogen-isotope permeation barrier. Electron-microscopy-based imaging and energy-dispersive X-ray spectroscopy measurements, together with X-ray diffraction experiments, indicate a sound film quality. We also measured deuterium permeation in the film at high temperatures ranging from 600 °C to 800 °C. The permeation reduction was most apparent at 650 °C. Above 800 °C, we confirmed that the film was damaged and did not work as a permeation barrier.

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I. INTRODUCTION

The deuterium and tritium isotopes of hydrogen are fuels for nuclear fusion experiments. In the fusion fuel delivery and storage systems, such hydrogen isotopes can permeate through the fuel lines and can be released outside during the operation of a nuclear fusion reactor, which is an environmental issue. Coated metal-oxide (M-O) films can reduce fuel permeation because the permeation process in M-O films is different from that in bare stainless steels. Hydrogen is known to permeate easily through SS fuel lines by thermal diffusion. However, when hydrogen atoms meet the surface of a M-O film, the hydrogen atoms tend to break M-O bond and form H-O bond until they replace all of the M-O bond [1,2]. Normally, the M-O bonding energy is larger than the H-O bonging energy. For the lengthening of the permeation process, large bonding energy difference between the M-O and H-O bonds is desired. To date, an Al$_2$O$_3$ film coating is known to be an excellent permeation barrier. However, in recent years, an Er$_2$O$_3$ film has been suggested to be a good candidate [2,3] for replacing Al$_2$O$_3$ film as a permeation barrier because an Er$_2$O$_3$ film can be easily obtained and has a large M-O binding energy in comparison to an Al$_2$O$_3$ film. In this regard, various Er$_2$O$_3$ coating techniques and substrate materials have been widely adopted to enhance hydrogen-isotope permeation reduction [2–10]. In recent years, theoretical calculations on hydrogen permeation through grain boundaries on M-O films by using ab initio density functional theory have been reported and have indicated that proper analysis of the microstructures of M-O films is essential to an understanding of the hydrogen permeation mechanism [7].

In this study, we tried to deposit an Er$_2$O$_3$ film on a type 316L stainless-steel (SS316L) substrate by using a chemical vapor deposition (CVD) technique. We obtain a 480-nm-thick Er$_2$O$_3$ film, which shows an appreciable permeation reduction factor (PRF) for deuterium at temperatures below 700 °C. With increasing temperature above 700 °C, the PRF is reduced drastically due to the fast activation of the Er$_2$O$_3$ film. We will discuss the structural and the permeation properties of the coated Er$_2$O$_3$ film in the next sections.

II. EXPERIMENT

A schematic of the CVD system used for this study is shown in Fig. 1. A 50-mm-diameter and 600-mm-long quartz tube was used as the main reactor chamber. The quartz reactor is surrounded by a heater that can heat the reactor to 1200 °C. A 20-mm-diameter 1-mm-thick SS316L coin-shaped substrate was located on a quartz substrate holder, which is located at the reactor center at a vertical angle of 30°. The substrates were carefully polished to a mirror finish by using a lapping machine. Before being coated, the substrates were heat treated at 700 °C in the reactor in a hydrogen atmosphere to removed the surface contaminants.
Fig. 1. (Color online) (a) A schematic drawing of the CVD system used for this study, in which the precursor and O\textsubscript{2} flows, the temperature and the base pressure of the growth chamber were precisely controlled. (b) A schematic drawing of the home-built hydrogen permeation measurement system (HPMS). The heating system is surrounded by a large volume vacuum thermal barrier to avoid temperature fluctuation during the permeation measurements.

Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) erbium, or simply Er(tmhd)\textsubscript{3}, was used as a precursor for the Er\textsubscript{2}O\textsubscript{3} coating. The Er(tmhd)\textsubscript{3} precursor is known to be stable while being transported from the sublimator, but is quickly decomposed to form Er\textsubscript{2}O\textsubscript{3} at temperatures above 500°C in an oxygen atmosphere. The sublimator and the transport tubes are composed of stainless steel and were wrapped with heater stripes. Thermal insulating materials were wound around the whole units, including sublimator, transport lines and heater stripes to reduce the temperature fluctuation during the process. High purity Ar gas was used as a precursor carrier and was regulated at a flow rate of 50 sccm by using mass-flow controller (MFC). After having passed through the MFC, the Ar gas was heated to 180°C. Therefore, the sublimated precursor’s temperature was maintained at 180°C in the sublimator and the transport lines. The flow rate of O\textsubscript{2} gas was 100 sccm. During the coating process, the pressure inside the reactor was maintained at 10 mbar by using an automatic pressure regulating valve mounted between the chamber and the vacuum pump. The total deposition time was 4 h, and after the film deposition process had been finished, samples were slowly cooled at a rate of 0.5°C/min. to room temperature. One thing of note is the clogging of the precursor in the precursor transport line after the film growth. Even though Er(tmhd)\textsubscript{3} is known to be a stable precursor, a significant amount of the precursor was deposited inside the transport line. Such precursor clogging in the transport line not only lengthened the coating time but also deteriorated the sample’s quality. Therefore, the used transport line had to be replaced with a new one after every deposition.

The Er\textsubscript{2}O\textsubscript{3} film’s thickness was measured to be 395 nm by using an ellipsometer (Woolim Model M-2000). For further analysis of the coated Er\textsubscript{2}O\textsubscript{3} film, we performed scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and X-ray diffraction (XRD) measurements. To obtain the deuterium permeation, we used a home-built hydrogen-isotope permeation measurement system (HPMS). Figure 1(b) shows a schematic diagram of the HPMS, which consists of a sample mount, a heater, and residual gas analysis (RGA) modules. The deuterium gas pressure was maintained at 1 bar during the permeation measurements. To minimize the sample’s temperature fluctuation, we located a heater unit in the vacuum chamber as a thermal shield. The partial pressure of deuterium on the permeate side, which was converted to the permeability of deuterium, was monitored.

Fig. 2. (a) SEM image of the as-grown sample before the permeation measurements. It shows granular-shape polycrystals with an average grain size of ~30 nm. (b) SEM image of the sample after the permeation measurements. Due to high temperature exposure, the film is seen to have been damaged.
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Fig. 3. (Color online) X-ray diffraction patterns of the SS316L bare substrate (bottom) and of the as-grown Er₂O₃ film on a SS316L substrate before and after the permeation experiments.

Table 1. Permeation reduction factors at different temperatures

| Temp. (°C) | 600  | 650  | 700  | 750  | 800  |
|------------|------|------|------|------|------|
| From Ref. 2 | 291  | 235  | 151  | -    | -    |
| This study  | 592  | 881  | 510  | 76   | 23   |

by using the RGA. The detailed development and operation procedure of the HPMS can be found elsewhere [11, 12].

III. RESULTS AND DISCUSSION

By using SEM and EDS, we obtained surface images and atomic compositions of the sample before and after the permeation measurements. Figure 2(a) exhibits an SEM image of a fresh as-grown Er₂O₃ film before the permeation measurements. It shows granular-shaped grains with an average size of 35 nm. After the high-temperature permeation measurements at 850 °C, as seen in Fig. 2(b), the average grain size was increased to ~50 nm. However, the film was damaged and no longer worked as a permeation barrier at this elevated temperature.

The EDS analysis showed that the atomic percent contents of O and Er were 43.8% and 22.7%, respectively, for the as-grown sample before the permeation experiments. The residual 33.5% comes from the substrate (SS316L). The content ratio of O to Er was 1.93, which was higher than the stoichiometric ratio of 1.5 due to the surplus oxygen content. After the permeation experiments, the atomic percents of O and Er were changed to 34.1% and 17.0%, respectively. In this case, the atomic content ratio of O to Er was 2.0. Exposure to high-temperature deuterium may reduce the amounts of O and Er. The similar contents ratios before and after the permeation measurements suggest that the surplus oxygen content may come from the native oxide formed on the SS316L surface. Even though the sample was exposed to high-temperature deuterium, it did not affect the native oxide on the surface of the SS316L substrate, which does not alter the O to Er content ratio.

The XRD spectra of the Er₂O₃ film and the SS316L substrate are displayed in Fig. 3. The peaks at 50.7° and 74.6° are from FeCrNiC SS316L substrate. The peak at 43.6° is the combined peak of the Er₂O₃ (431) and the SS316L (111) planes, and all other peaks can be indexed to Er₂O₃. As seen in the figure, intensities of the XRD peaks of Er₂O₃ became sharper (smaller line widths) and stronger after the permeation experiments compared with those of the as-grown sample. This is due to the improvement in the crystallinity caused by the long-term exposure at high-temperature during the permeation experiments. However, even though the crystallinity had been improved, the Er₂O₃ film was significantly damaged due to the large mismatch of the thermal expansion coefficients between the substrate and the coated film at such a high temperature, as seen in Fig. 2(b).

Arrhenius plots of the deuterium permeabilities for both the base and the Er₂O₃-coated SS316L samples are displayed in Fig. 4. Solid square markers are the data measured in this study. To compare our permeability data with those of other research groups using a similar deposition technique, we display data extracted from Ref. 2 as circular markers. The permeability was recorded when deuterium permeation reached the steady state. We measured the permeability at five different temperatures from 600 °C to 800 °C by 50 °C steps. As seen in the figure, the permeability increases with increasing temperature. Below 700 °C, the slope and the amount of the permeability are moderate and small,
respectively. However, above 700 °C, the permeability slope rapidly increases. In comparison, the values measured in this study are significantly lower than the values from Ref. 2 (solid circle). The permeation reduction factor (PRF), which is the ratio of the permeability of SS316L to that of Er₂O₃, is summarized in Table 1. A larger PRF value indicates better permeation protection. The PRF at 600 °C is 592, which increases to 881 at 650 °C, and then decreases to 510 at 700 °C. The reason for such a sudden increase in the PRF at 650 °C is not clear. One plausible explanation can be an annealing effect. As mentioned above, the permeability values were recorded at the steady state, and it can take hours to days to reach the steady state, depending on the designated temperature. During the 600 °C and 650 °C measurements, the sample was exposed several hours at such an elevated temperature exceeding the growth temperature, and the improved crystallinity of the sample during the measurements may have caused the increase in the PRF at 650 °C.

**IV. CONCLUSION**

We fabricated an Er₂O₃ film on a SS316L substrate by using a CVD method. After a 4-hour growth, the film thickness was measured to be 395 nm by using an ellipsometer. SEM images taken after the deuterium permeation measurements at 850 °C indicated that grains with an average size of ~30 nm for an as-grown polycrystal film became large enough to induce crack damage. By using a home-built HPMS, we measured the deuterium permeability of the Er₂O₃ film at temperatures between 600 °C and 800 °C in 50 °C steps. The measured permeation reduction was most apparent at 650 °C. Above 700 °C, the permeability decreased rapidly with increasing temperature, and at 850 °C, the film was damaged and no longer worked as a permeation barrier.

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**REFERENCES**

[1] R. W. Lee, R. C. Frank and D. E. Swets, J. Chem. Phys. 36, 1062 (1962).
[2] Y. Wu et al., Int. J. Hydrogen Energy 41, 431 (2016).
[3] D. Levchuk et al., J. Nucl. Mater. 367–370, 1033 (2007).
[4] Z. Yao et al., J. Nucl. Mater. 386–388, 700 (2009).
[5] S. Liu et al., Fusion Eng. Des. 85, 1401 (2010).
[6] T. Chikada et al., J. Nucl. Mater. 442, 533 (2013).
[7] W. Mao et al., J. Nucl. Mater. 443, 555 (2013).
[8] T. Chikada et al., Fusion Eng. Des. 89, 1402 (2014).
[9] J. Wang et al., Int. J. Hydrogen Energy 41, 1326 (2016).
[10] Q. Li, J. Wang et al., J. Eur. Ceram. Soc. 37, 249 (2017).
[11] S. K. Lee, S-H. Yun, H. G. Joo and S. J. Noh, Curr. Appl. Phys. 14, 1385 (2014).
[12] H. S. Kim, W. J. Byun and S. J. Noh, J. Korean Phys. Soc. 72, 1 (2018).