Measurement of hydrogen isotope concentration in erbium oxide coatings

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HIGHLIGHTS

- We measure hydrogen isotope concentration in erbium oxide coatings.
- Hydrogen isotope adsorption on the coating is observed.
- Deuterium forms a chemical bond with carbon in sample fabricated by metal organic decomposition.
- High grain-boundary area density increases deuterium concentration.
- Deuterium concentrates in particular place which seems grain-boundary.

ARTICLE INFO

ABSTRACT

Hydrogen isotope concentrations in erbium oxide coatings fabricated by filtered arc deposition and metal–organic decomposition have been investigated using nuclear reaction analysis and secondary ion mass spectroscopy. It was found that the deuterium concentration in the coatings fabricated by filtered arc deposition was 300–500 atomic parts per million, whereas the deuterium concentration in the coating fabricated by metal–organic decomposition was approximately 2.0×10^4 atomic parts per million due to hydrogen trapping by carbon impurities. Deuterium concentrations in the coatings fabricated by filtered arc deposition increased with increasing depth in accordance with the increase of grain boundary area density. An in-plane deuterium distribution of the coating by secondary ion mass spectroscopy proved segregation with a net-like structure, indicating that the deuterium diffused through the grain boundaries.

1. Introduction

Tritium handling has been studied for a long period of time in an effort to establish a safe and efficient fuel cycle in fusion reactors. Since candidate structural materials generally exhibit high permeability of hydrogen isotopes in the operational temperature range, it is essential to suppress tritium permeation through pipe walls. For many years, ceramic coatings have been developed as one method of reducing tritium permeation [1,2].

Erbium oxide (Er_2O_3) coatings have recently been studied as one of the most promising tritium permeation barrier (TPB) materials [3–7]. Hydrogen isotope permeation experiments on the Er_2O_3 coatings have been conducted under various conditions to clarify the permeation mechanism. A series of investigations revealed that Er_2O_3 coatings fabricated by filtered arc deposition significantly reduce permeation. It has also been reported that a multilayer structure significantly decreases deuterium permeation by increasing the number of permeation steps: solution and diffusion [7]. The hydrogen diffusion behaviors of Er_2O_3 coatings have been discussed in several papers, whereas no information on their hydrogen solution behaviors has been provided. Tritium concentration in the coatings has a significant influence not only on the permeation behavior but also on tritium inventory in blanket systems.

In the present research, hydrogen isotope depth profiles of Er_2O_3 coatings were measured using nuclear reaction analysis (NRA) with tandem accelerators. NRA is a proven method for investigating tritium inventory in diverter materials such as tungsten [8,9]. Additionally, in-plane deuterium distributions have been examined by nanoscale secondary ion mass spectroscopy (SIMS). Nanoscale SIMS provides two-dimensional (2D) mapping of elements, which

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has been helpful in determining the diffusion paths of oxygen in ceramics [10]. The goal of the current study is to examine hydrogen isotope concentrations in Er_2O_3 coatings fabricated using filtered arc deposition and metal–organic decomposition through these analyses for a better understanding of tritium behavior.

2. Experimental details

2.1. Coating methods

Reduced activation ferritic/martenstic (RAFM) steel F82H (8Cr-2W, Heat No. 9753 42W-4) was used for the substrate material. Square plates (25 mm × 25 mm, 0.5 mm thick) were mirror polished. Er_2O_3 coatings were fabricated by two methods: filtered arc deposition and metal–organic decomposition (MOD), as detailed in Refs. [5,6].

For the filtered arc deposition, an arc current was applied on an erbium metal cathode (99.9% Er) with filtering of the plasma from metal droplets. Oxygen was introduced into the main chamber, forming an Er_2O_3 coating. During the deposition, an RF-induced bias voltage of −150 V was applied on the sample to enhance crystallinity [11]. 1.4-μm-thick coatings were deposited on one side or both sides of the substrate.

The coating procedure for the MOD method includes the following steps: (1) the substrate was pulled up from a liquid precursor at a constant speed of 1.2 mm s^{-1}, (2) dried in a drying oven at 120 °C for 15 min, and (3) heat treated to crystallize the Er_2O_3 coating. The heat treatment conditions were 550–700 °C for 10 min under high-purity hydrogen with 0.6% water vapor. Coatings with thicknesses of less than 100 nm were fabricated on one side of the substrate.

2.2. Introduction of hydrogen isotopes

Hydrogen isotopes (protium and deuterium) were introduced into the coated samples at 400, 500, and 600 °C using the hydrogen isotope permeation apparatus described in Ref. [12]. Two chambers divided by a sample were separately evacuated up to 10^{-6} Pa. Hydrogen isotopes were introduced into one side (called the upstream side) at a pressure of 8.00×10^4 Pa. The partial pressure of the hydrogen isotopes in the other chamber (called the downstream side) was measured by a quadrupole mass spectrometer (QMS). The downstream side was continuously pumped out to a pressure of less than 10^{-4} Pa during the experiments. The sample coated on one side was mounted with the coated side facing the upstream side in order to avoid surface oxidation on the uncoated side of the sample by contamination molecules in the chamber.

The procedure for introducing hydrogen isotopes is described as follows. First, a hydrogen permeation experiment was performed at 600 °C for 17 h on all samples to standardize their microstructure because a phase change of Er_2O_3 during the first permeation experiment was reported in our previous study [13]. After the permeation test, the upstream chamber was evacuated to release the hydrogen isotopes from the sample. The hydrogen isotopes were then reintroduced into the sample at 400 or 500 °C. When the steady-state permeation flux was achieved, the sample was rapidly cooled to room temperature at a rate of approximately 15 °C min^{-1} to retain the hydrogen isotopes in the sample while maintaining the upstream pressure. For the hydrogen isotope introduction at 600 °C, the sample was rapidly cooled down after the 17 h permeation test. Each sample was labeled to indicate the coating method and introduction temperature, such as "Arc-400" and "MOD-500." Samples coated on both sides were denoted with "b" before the introduction temperature, such as "Arc-b600."

2.3. Measurement of hydrogen isotope concentration distribution by nuclear reaction analysis

NRA procedures for protium and deuterium are explained in detail in Refs. [14,15]. A probing beam of ^{15}N or ^3He with diameters of approximately 3 mm and 1 mm, respectively, was injected into the sample. The ion beam reacted with the hydrogen elements and ejected particles or photons. In order to probe the hydrogen depth profiles in the coatings, the incident beam energy was changed from 6.3 MeV to 9.8 MeV for ^{15}N and from 0.69 MeV to 4.0 MeV for ^3He.

For the examination of protium concentration, a nuclear reaction of $H(^{15}N, \gamma\alpha)^{12}C$ was performed by a tandem-type Van de Graaff accelerator at the Micro Analysis Laboratory, Tandem accelerator (MALT) at the University of Tokyo [11]. The protium concentration was determined via γ-ray intensity using a semiconductor detector. The γ-ray intensity was divided by an ion beam current for normalization and converted to protium concentration using a standard sample, Kapton® polyimide film. A nuclear reaction with a very narrow resonance width of 1.8 keV occurred at a collision energy of 6.385 MeV-^{15}N beam against the surface protium.

In order to obtain deuterium profiles, ^3He was irradiated by a tandem accelerator at Max-Planck-Institut für Plasmaphysik (IPP), Garching, Germany, as explained elsewhere [15]. The deuterium concentration was determined using a proton detector via a reaction of $D(^3He, p)^4He$. The resonance width of this reaction was approximately 500 keV. Therefore, the spectra were deconvoluted using the SIMNRA code [16]. The proton intensity was also normalized by ion beam current and converted to deuterium concentration using a standard sample of amorphous deuterated hydrocarbon (a-C:D). Additionally, Rutherford backscattering spectrometry (RBS) was performed at the same time with the equipment at IPP-Garching, which provided the thickness and composition of the Er_2O_3 coating.

2.4. Deuterium 2D mapping by nanoscale secondary ion mass spectroscopy

SIMS was applied to obtain deuterium 2D mappings for Arc-b500 and MOD-500. Each sample was cut into small pieces (7 mm × 7 mm) and coated with gold to suppress the charge-up effect. Mass spectra and depth profiles for protium, deuterium, carbon, and oxygen were measured using the Cameca NanoSIMS50 ion microprobe (Cameca, Courbevoie, France) described in Ref. [10]. Cs$^+$ primary ions were irradiated into the samples as a tightly focused ion beam with a probe working diameter. The secondary ions were guided through several transfer lenses to the entrance of a mass spectrometer. During the measurement of the depth profiles, the intensities were collected as a function of sputtering time.

3. Results

3.1. Thickness and chemical composition of Er_2O_3 coatings

The coating thickness and Er composition fraction were measured for Arc-400, Arc-b400, Arc-b500, Arc-b600, and MOD-500 by RBS. The Er fractions of the samples fabricated by the filtered arc deposition were 40%, corresponding to the stoichiometric composition of Er_2O_3. By contrast, the Er fraction in MOD-500 showed a very low value of approximately 15%.

3.2. Protium concentration profile

Fig. 1 shows protium concentration profiles of MOD-400, Arc-500, and Arc-600. The protium was detected near the surface of the Er_2O_3 coating and retained by 40 at% in MOD-400 and