Deuterium diffusion in a chemical densified coating observed by NRA

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ABSTRACT

Ceramic coatings on structural material are expected as a barrier for tritium permeation in fusion devices. A Cr_2O_3–SiO_2–$CrPO_4$ coating on stainless steel by use of a chemical densified coating (CDC) method was experimentally studied. The sample disk was exposed to a deuterium plasma and an analyzing beam of ^{3}He ions irradiated the sample to observe deuterium concentration profiles. It was found that a very long time, typically 10 ks at 563 K, was needed for deuterium to diffuse from the surface to a few μm in depth. The profiles were analyzed with a diffusion model to obtain the diffusion coefficient of deuterium, which was expressed by $1.1 \times 10^{-10} \exp(-0.71 \text{ eV}/kT)$ [$m^2 s^{-1}$] between 470 and 723 K. The diffusion coefficient was about 5 orders of magnitude smaller than that in type 304 stainless steel at 563 K. The CDC coating is expected to significantly delay tritium permeation.

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1. Introduction

Ceramic coatings on a metal surface are an effective way to reduce tritium permeation through blanket components in a fusion device [1]. Chemical densified coating (CDC) is suitable for a metal tube because it is capable of forming coatings on the inner surface of the tube and its low process temperature does not affect properties of the stainless steel tube material [2]. The CDC method, however, has the disadvantage that the coating is somewhat porous, allowing tritium to pass through.

Recently, Nakamichi et al. [3] developed an advanced CDC method for employing densification treatment with $CrPO_4$ on a Cr_2O_3–SiO_2 coating. They conducted a permeation experiment and showed that the CDC coating fabricated by this method had a good barrier performance. Quantitative evaluation, however, has not been made since permeation was not detected.

In Nakamichi's experiment, hydrogen diffusion in the CDC coating was considered to be very low, such that no hydrogen could reach the opposite side of the sample membrane. In the present work, the diffusion coefficient of hydrogen isotopes was estimated by another method, in situ deuterium observation by use of nuclear reaction analysis (NRA). The NRA adopted in the present work is a non-destructive method for measuring deuterium concentration profiles from the surface to a few μm in depth, from which diffusion coefficients can be estimated with an appropriate diffusion model.

2. Experimental set-up

The sample was a disk of 304 stainless steel with a diameter of 34 mm and a thickness of 2 mm. One side of the sample was coated with Cr_2O_3–SiO_2 by the CDC method and subsequently treated with $CrPO_4$, which has been described elsewhere as a Type 2 coating [3]. The thickness of the coating was 50 μm.

The sample was set on a holder in a vacuum chamber and heated by an ohmic heater, as shown in Fig. 1. The sample temperature was measured by a thermocouple. In order to charge deuterium into the sample, the coating side of the sample was exposed to a deuterium plasma produced by radio frequency (rf) in a discharge tube. The deuterium gas pressure in the tube and the rf power were kept constant at around 1 Pa and 20 W, respectively, during the whole experiment.

The depth profiles of deuterium on the coating side were observed by the NRA with the reaction of $D(^3\text{He}, p)^4\text{He}$. An analyzing beam of 1.7 MeV ^{3}He$^+$ ions was accelerated by the 4 MV Van de Graaff Accelerator at Kyoto University and irradiated the sample at an incident angle of 45° through two hole-slits of 4-mm diameter. Protons produced in the sample were detected by a solid state detector (SSD) located at a scattering angle of 174.3°.

The energy spectrum of protons was converted into the depth profile of deuterium by the energy analyzing method [4]. In the conversion, projectile ranges of ^{3}He in the sample material were needed. The range in $CrPO_4$ is not very different from SiO_2, but is about 40% larger than that in Cr_2O_3. As the composition of the sample material was not exactly known, the range in $CrPO_4$ was used representatively since the surface of the sample mainly consisted of $CrPO_4$ [3].
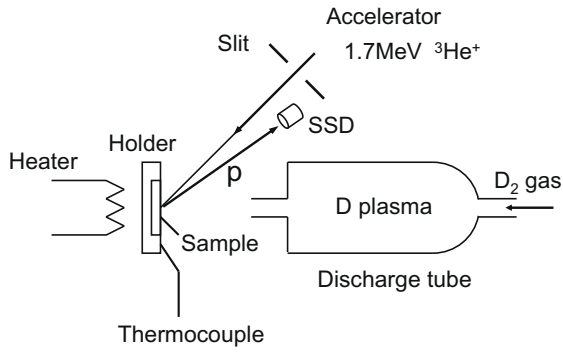
Fig. 1. Schematic drawing of the experimental set-up.

As the deuterium partial pressure in the vacuum chamber was very low (5 mPa), protons produced in the gas phase scarcely contributed to the spectrum. The beam flux was 1.2×10^{16} m^{-2} s^{-1}, which caused no increase in the sample temperature. The time for each NRA was 1.8 ks.

3. Results and discussion

A typical depth profile is shown in Fig. 2, in which the sample temperature was 563 K and the elapsed time from the start of the plasma exposure was 11.7 ks. Due to the finite resolution of the measuring system, deuterium seemed to exist at a negative depth in the figure. The probe depth was around 2 μm. Note that the elapsed time was a median between the start and the end time of the NRA. In the experiments, the measurement time of 1.8 ks was generally much smaller than the elapsed time.

The depth profile can be divided into two parts: a peak at 0 depth and a gradual slope downward to deeper depths in the bulk. The peak is attributed to deuterium atoms on the surface [5]. The kinetic energy of deuterium particles from plasma is as low as a few eV [6]; therefore, the particles are not implanted into the bulk region, but absorbed on the surface. As the result, the areal density of deuterium, S, rapidly increases to reach a constant value soon after plasma exposure.

The gradual slope in the profile is attributed to deuterium in solution sites, which can diffuse into the bulk. As deuterium atoms in the bulk move from the surface, where they are absorbed, the concentration of deuterium in solution sites just beneath the surface, $C(0, t)$, can be taken as a constant value of C_0 at any time, t. The opposite side of the sample is very far from the plasma exposure side so the deuterium is considered to diffuse in a semi-infinite media through the one-dimensional direction x. The analytical form of the diffusion equation under the above conditions and an initial condition of $C(x, 0) = 0$ is [7],

$$C(x, t) = C_0 \left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}} \right) \right], \tag{1}$$

where D is the diffusion coefficient.

In the analysis, C_0 is estimated from the slope of the profile extrapolated to 0 depth and the areal density, S, is taken from the peak area of the profile. A depth resolution, represented by a full width at half maximum of 400 nm is applied to both S and $C(x, t)$. Thus, D is a main fitting parameter.

Fig. 2 shows the calculated result of S, $C(x, t)$ and their total, which well reproduces the experimental profile. At the sample temperature of 563 K, the profiles were observed at 11.7, 22.5 and 44.1 ks. These profiles can be reproduced by the calculation with the same diffusion coefficient of 6.0×10^{-17} m^2 s^{-1}, which indicates deuterium atoms move in the sample by the diffusion process.

The same experiment was conducted under different temperature conditions of 470–723 K. The sample was altered differently at each temperature. The results of the analysis are summarized in Table 1.

The areal density S does not depend on the elapsed time because it rapidly increases due to the absorption process. In addition, S seems to be nearly independent of the sample temperature, which indicates that the absorption sites for hydrogen were nearly saturated under the present experimental conditions. The atomic surface density of solids is around 2×10^{19} m^{-2} and much smaller than S of 1×10^{21} m^{-2}. One reason for this large discrepancy may be surface roughness. The depth resolution was 160 nm in the case of nickel samples [5], for which the surface was considered to be flat. The depth resolution of 400 nm in the present work indicates that the sample surface was very rough and hence the effective area of the surface was very large.

The concentration of deuterium, C_0, was nearly constant and did not depend on the elapsed time under the same temperature. This result is reasonable because deuterium atoms in solution sites come from the surface and the amount of S is constant. The temperature dependence of C_0 was not clear due to the large scattering
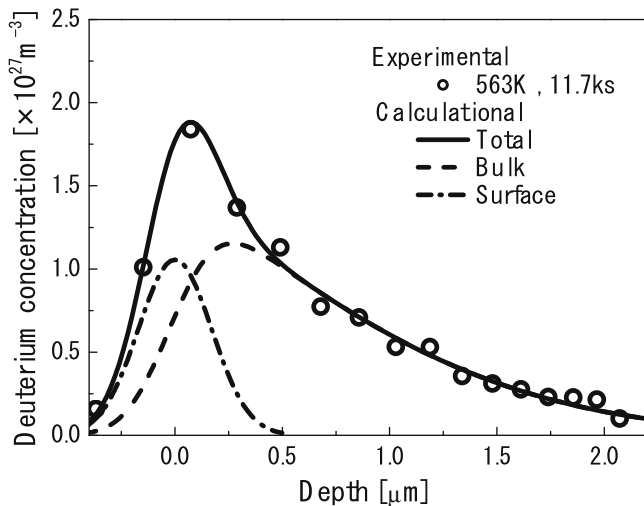

Fig. 2. A deuterium depth profile at a temperature of 563 K and elapsed time of 11.7 ks. Lines are results of the calculation with a diffusion model.

Table 1
Results of the deuterium areal density S, the concentration just beneath the surface C_0 and the diffusion coefficient D at temperature T.

| T (K)	t (ks)	S (m^{-2})	C_0 (m^{-3})	D (m^2 s^{-1})
470	208	1.2×10^{21}	5.5×10^{26}	3.0×10^{-18}
	300	0.7×10^{21}	8.0×10^{26}	3.0×10^{-18}
	(Average)	1.0×10^{21}	6.8×10^{26}	3.0×10^{-18}
520	11.7	4.5×10^{20}	1.5×10^{27}	1.5×10^{-17}
	22.5	5.0×10^{20}	1.8×10^{27}	1.5×10^{-17}
	44.1	8.5×10^{20}	2.0×10^{27}	1.5×10^{-17}
	(Average)	6.0×10^{20}	1.8×10^{27}	1.5×10^{-17}
563	11.7	4.5×10^{20}	1.6×10^{27}	6.0×10^{-17}
	22.5	6.0×10^{20}	1.7×10^{27}	6.0×10^{-17}
	44.1	6.0×10^{20}	1.7×10^{27}	6.0×10^{-17}
	(Average)	5.5×10^{20}	1.7×10^{27}	6.0×10^{-17}
630	11.7	1.0×10^{21}	7×10^{26}	3.0×10^{-16}
	22.5	1.0×10^{21}	7×10^{26}	3.0×10^{-16}
	44.1	1.0×10^{21}	9×10^{26}	3.0×10^{-16}
	(Average)	1.0×10^{21}	8×10^{26}	3.0×10^{-16}
723	3.0	1.2×10^{21}	2.7×10^{27}	1.0×10^{-15}
	6.8	1.2×10^{21}	2.5×10^{27}	1.0×10^{-15}
	(Average)	1.2×10^{21}	2.6×10^{27}	1.0×10^{-15}
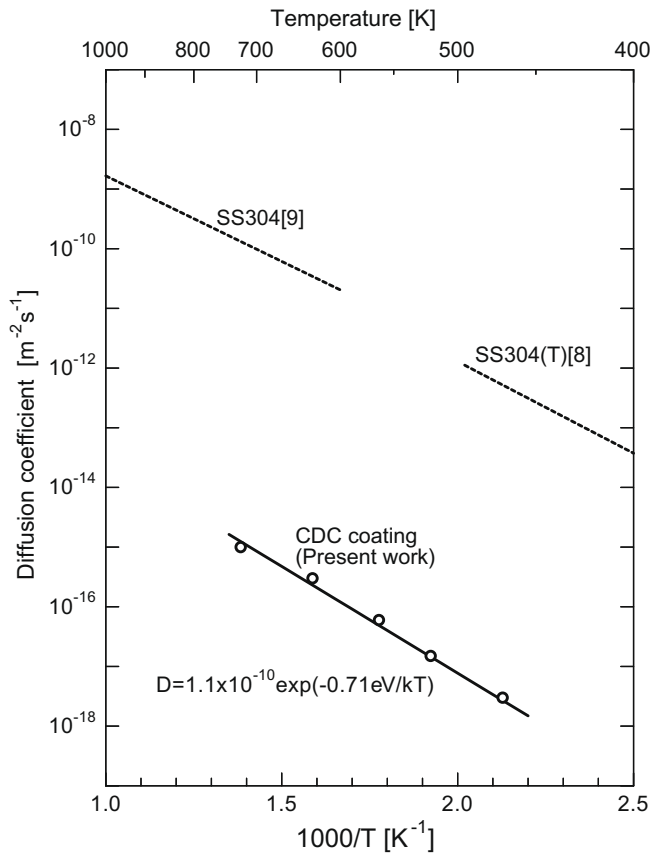
Fig. 3. Diffusion coefficient of deuterium in the CDC coating and in type 304 stainless steel.

of the data. As C_0 is an extrapolated value, it essentially contains some uncertainty. Similar to S, C_0 is also considered to be independent of the sample temperature.

The diffusion coefficient, D, strongly depended on the sample temperature, as shown in Fig. 3. The data can be expressed by an Arrhenius relation of

$$D = 1.1 \times 10^{-10} \exp(-0.71 \text{ eV} / kT) \quad [\text{m}^2 \text{ s}^{-1}]. \tag{2}$$

The diffusion coefficients in type 304 stainless steel [8,9] are also shown in Fig. 3. Deuterium diffused into the CDC coating very slowly and the rate of diffusion was much smaller than that in stainless steel; for example, the diffusion coefficient at 563 K was about 5 orders of magnitude smaller. It is expected that the CDC coating significantly delays tritium permeation when it is coated on a metal surface, such as stainless steel. For more a quantitative evaluation, hydrogen solubility is needed since the amount of permeation depends on not only diffusion, but also solubility.

4. Summary

The deuterium depth profiles in a CDC coating continuously exposed to the deuterium plasma were observed by the NRA method. The profile consisted of two parts, that is, the surface peak of absorbed deuterium and the bulk slope of diffusive deuterium. The latter was analyzed with a one-dimensional diffusion model. It was found that (1) the surface density became constant soon after the plasma exposure and did not depend on the sample temperature, and (2) deuterium in the solution site diffused very slowly in the bulk; for example, the diffusion coefficient was 6.0×10^{-17} $\text{m}^2 \text{ s}^{-1}$ at 563 K. The CDC coating is expected to significantly delay tritium permeation.

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