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Effect of surface oxide layer on deuterium permeation behaviors through a type 316 stainless steel

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ABSTRACT

Effect of surface oxide layer on the hydrogen isotope permeation was studied. Iron oxide was uniformly formed in the oxide layer, although chromium was limited at the interface between the oxide layer and bulk SS-316. The permeation behavior of deuterium for oxidized SS-316 was compared with that for unoxidized SS-316 at temperature range of 333–673 K. The deuterium permeability for the oxidized SS-316 was reduced 1/10–1/20 times as high as that for unoxidized one. However, the activation energy of deuterium permeation as gas form for oxidized SS-316 was almost the same as that for unoxidized SS-316 and was 0.64 eV, which was almost consistent with the sum of activation energies for diffusion and solubility. This fact indicates that the deuterium permeation is diffusion limited. The permeability of deuterium as water form was almost constant even if heating temperature is high, showing that the deuterium was permeated through bulk SS-316 and react with oxygen at the oxide layer as water desorption, which is controlled by the permeation flux of deuterium and oxygen concentration on the surface of oxide layer in downstream side.

1. Introduction

The type 316 stainless steel (SS-316) is used in fusion reactors as various component materials due to their good mechanical properties and corrosion resistance, and is thought to be exposed to hydrogen isotopes including tritium [1–5]. It is well known that the oxide layer on the stainless steel is one of the key tritium diffusion and permeation boundary and various researches are devoted for several years [1–5]. In our studies [6–8], the deuterium or heavy water was desorbed on the sample by various methods, such as water adsorption, ion irradiation and electrolysis, and it was found that the metal oxide and oxyhydroxide, FeOOD or CrOOD, were formed on the surface and the dominant chemical state was changed by the absorption method. The deuterium retentions for oxidized SS-316 at various temperatures were also evaluated [8]. The deuterium retention trapped by the oxide layer, which corresponded to the desorption temperature of 600–800 K, was governed by the ratio of oxide layer, especially iron hydroxide. All of the iron was not oxidized and the saturation ratio of iron oxide to pure iron existed in the stainless steel, which indicated that the saturation of deuterium retention trapped by the oxide layer was controlled by the amount of iron oxide in the oxide layer.

For the assessment of fusion safety, the evaluation of tritium permeability is required to reduce environmental impact and human radiation safety. Therefore, tritium permeation through the stainless steel will be one of conceivable risks in fusion reactors. It can be said that control of permeation and elucidation of tritium recovery behaviors are quite important for fusion safety. Many researches have been carried out about permeation behaviors of hydrogen isotopes through stainless steels [1–5]. However, hydrogen isotope permeation experiments under lower temperature have been limited because of difficulties in measurement caused by lower permeation rate. In addition, it is considered in lower temperature that surface effects for the oxide layer on the stainless steels would impact on the permeation behavior, especially permeability of tritium and chemical form of permeated tritium. Thus, Tritium Permeation-Recovery System (T-PRES) has been established at Shizuoka University for the evaluation of permeability and permeation amount to elucidate the permeation mechanism of tritium in SS-316. The permeation behavior of deuterium for oxidized SS-316 was compared with that for unoxidized SS-316 at temperature range of 333–673 K.

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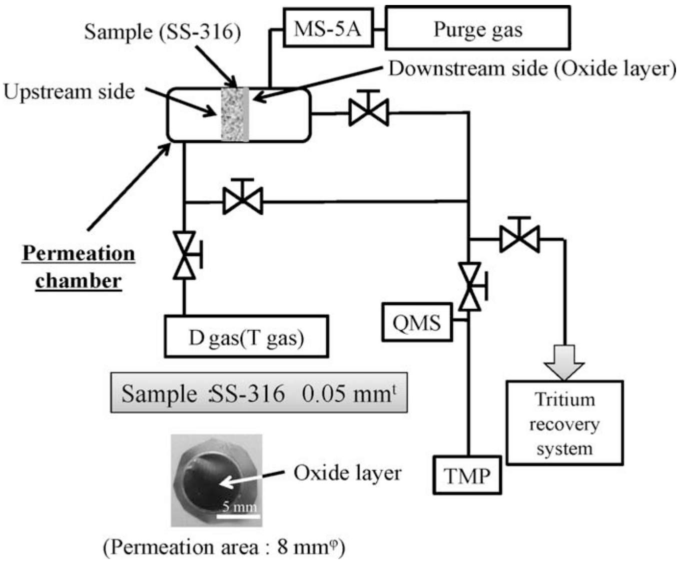

Fig. 1. Schematic drawing of experimental setup.

2. Experimental

The 8 mm^{φ} × 0.05 mm^{t} of SS-316 purchased from Nilaco Inc. was used as a sample. The sample was evacuated by turbo molecular pump at the pressure less than 10^{-5} Pa. Then, the sample was heated at 1173 K for 1 h under keeping vacuum to remove the surface impurities and residual hydrogen on/in SS-316 and the sample oxidation for permeation side was performed by introducing Ar gas with 1000 ppm oxygen with the pressure of 0.2 MPa at 673 K for 50 h. Thereafter, the sample was transferred to the permeation experiment system. Fig. 1 shows the schematic drawing of experimental setup (Tritium Permeation-Recovery System (T-PRES)) for tritium permeation measurement. For the deuterium permeation experiment, the vacuum chambers for both of upstream and downstream side were evacuated at the pressure less than 10^{-5} Pa. After the evacuation, the sample was heated at the temperature between 333 K and 673 K and the pure deuterium gas was introduced in the upstream chamber with the pressure of 10 kPa for 1–40 h. After the permeation experiment, the amount of deuterium permeated through SS-316 was evaluated by a quadruple mass spectrometer (MKS E-VISION). The chemical states of oxidized SS-316 were evaluated by XPS (X-ray photoelectron spectroscopy) (ULVAC-PHI Inc.). The Ar^{+} sputtering technique was used for the evaluation of depth profiles of atomic concentration profiles. The unoxidized sample was prepared by heating treatment at 1173 K for 1 h under vacuum in the T-PRES and the surface oxide layer was completely removed, which was confirmed by XPS analysis.

3. Results and discussion

Fig. 2 shows the depth profiles of constituent atoms for the oxidized SS-316 observed by XPS. It was found that the oxide layer was formed with the thickness of 60–70 nm. In the oxide layer, the profile of chromium has a concentration gradient and its concentration was decreased toward the surface, although iron was uniformly distributed due to different diffusion coefficient for iron and chromium. This profile was almost consistent with our previous studies [8,9].

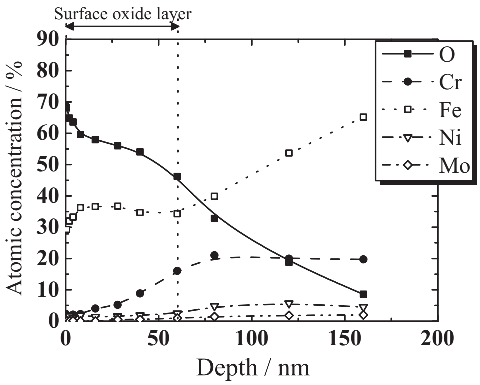

Fig. 2. Depth profiles of constituent atomic concentration for oxidized SS-316.

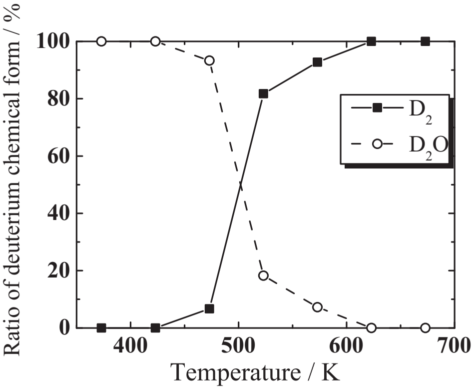

Fig. 3. Ratio of deuterium chemical form permeated through oxidized SS-316 at various temperatures.

Using this oxidized SS-316, the deuterium permeation experiments were performed. Fig. 3 shows the ratio of desorption chemical forms at various temperatures. The major chemical form of deuterium at higher temperature more than 500 K was deuterium gas form. However, heavy water was the major chemical form in the temperature less than 500 K, indicating that the most of deuterium permeated through SS-316 was oxidized on the oxide layer formed on the surface at downstream side in lower temperature. This figure shows that the major deuterium chemical form permeated through the oxidized SS-316 was controlled by the sample temperature. The permeability of total deuterium including gas and water forms as a function of heating temperature was shown in Fig. 4. The deuterium permeability clearly had good dependence on heating temperature above 500 K. However, in the lower temperature less than 500 K, the slope of permeability was reduced, indicating that the permeation behavior was clearly changed at the temperature of 500 K, which could be explained by deuterium diffusion in the grain boundary [3]. Based on the results of Figs. 3 and 4, the change of chemical form for

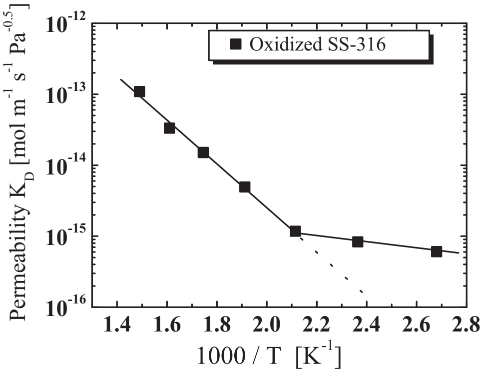

Fig. 4. Permeability of total deuterium both of gas and water forms as a function of heating temperature.