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Hydrogen absorption process into graphite and carbon materials

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Abstract

In order to estimate bulk hydrogen retention and recycling in graphite and carbon materials, molecular hydrogen absorption has been studied. Hydrogen absorption rates significantly depend on samples which arise from grain size, trap concentration and so on. Absorption rate constants differ between the cases of low and high pressures. Trapping has a strong influence, especially in the low pressure range. Oxidation of graphite reduces hydrogen retention and enhances the absorption rate. This suggests that oxygen in graphite does not behave as trapping sites for hydrogen. Activation energies for apparent diffusion for H_2 and D_2 are determined to be 153 and 158 kJ/mol. They are smaller than those energies determined from desorption measurements.

1. Introduction

Graphite and carbon-based materials are still principal candidates for plasma facing components, although the application of beryllium or high-Z materials is also attractive. For plasma facing materials in future devices such as ITER, a combination of carbon materials, beryllium and tungsten alloy has been designed as an answer to particular demands for each component [1–3]. As well known, carbon causes high hydrogen recycling and high tritium inventory. The authors have studied bulk hydrogen retention in connection with the microstructure of graphite and carbon materials [4–6]. In these papers, the authors show that bulk hydrogen retention significantly depends on the brands of graphite and CFC [6], and neutron irradiation leads to the enhancement of hydrogen retention and suppression of hydrogen mobility in these materials [5]. Based on suggestions [7,8] that oxygen may strongly reduce hydrogen and tritium retention in a codeposited layer on the plasma facing surface, gas oxidation or oxygen discharge has been applied for some devices to get lower hydrogen recycling and small tritium inventory [9–11]. However, the reaction of oxygen with carbon does not only change surface morphology but also may introduce trapping sites in the carbon for hydrogen similar to the case of beryllium [12,13] and tungsten [14,15]. It is reported that hydrogen in the near-surface region was desorbed from graphite and carbon-based material after oxidation at high temperatures [16,17]. Thus, the oxidation may affect diffusion paths for hydrogen in these materials.

In the present work, the following key issues to estimate hydrogen bulk retention and recycling have been investigated through hydrogen absorption experiments; namely, (1) hydrogen absorption rate into graphite and CFC, (2) oxidation and oxygen impurity effect on the absorption process and (3) the hydrogen isotope effect on the process.

2. Experimental

The samples used in this study were nine brands of graphite and CFC from six manufacturers, which are Toyo Tanso (IG-110U, IG-430U, ISO-880U and CX-2002U), Ibiden (ETP-10), Ringsdorff (EK-98), POCO

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Graphite (AXF-5Q1), Union Carbide (ATJ) and Le Carbone Lorraine (CL-5890PT). All materials are isotropic graphites, except CX-2002U which is a CFC material. These samples were outgassed at 1773 K for one hour below the pressure of 10^{-3} Pa before absorption experiments. The measuring apparatus has been improved from the system described in [18], where the initial stage of absorption can be monitored and very small retention can be determined. The detection limit is 1 s^{-1} as the highest absorption rate (D/r^2), and the lowest bulk hydrogen retention is 0.1 ppm. Hydrogen retention and absorption rates were evaluated from the pressure decrease in a constant volume system with a Baratron capacitance manometer (390 H, MKS). Pressure data were stored in a personal computer at every second during the initial stage, and subsequently every 10 s up to 30 h. The pressure range of experiments was below 40 kPa to avoid methane formation [18], where it makes pressure decrease in the system. Sample oxidation was performed at 973 and 1073 K for 2 h under dry airflow.

3. Results and discussion

3.1. Hydrogen absorption rate

In the hydrogen absorption measurements, equilibrium, where the pressure decrease terminates, was established in 0.5–20 h. The time depends on experimental conditions such as temperatures and pressures. Hydrogen absorption into the samples was analyzed with a diffusion-controlled process in a medium of spherical system. The system simulates graphite grains (diameter: 1–50 μm) [5], since the molecular hydrogen diffusion along the grain boundary, or through open pores, is rapid enough to assume that hydrogen pressure at each grain surface is same to the pressure outside the sample. The hydrogen pressure change fits the theoretical curve well, and the solubility constant S_0 (m^3 $Pa^{-1/2}$), here referred to as the hydrogen retention, and the absorption rate constant D/r^2 (s^{-1}) could be derived with the same way applied in [5]. Using the grain radius for r, the apparent diffusion coefficient, D, can be obtained. Since the graphite grain is not proved as a diffusing medium, and also grains have quite different size, r was not substituted into D/r^2.

The hydrogen absorption rate constants, D/r^2, at 1273 K determined for nine samples are shown in Fig. 1. The values differ significantly between the different samples, e.g., the difference between 5890PT and ISO-880U is 12 times. In fact, the time needed for equilibrium was 50 min for ISO-880U, while it was 3 h for 5890PT. The principal reason of the difference may come from the grain size, which was 5 μm for ISO-880U, 14 μm for IG-110U and 40 μm for ETP-10 (nominal data from manufacturers), although there is an inconsistency between IG-110U and ETP-10. Hence, the following two effects should contribute strongly as discussed later. The first is pressure dependence, in other words, the correlation between trap concentration and the number of offered hydrogen atoms per time. The second is the oxidation effect, which changes the diffusing path or trap concentration. These effects were investigated with IG-110U and the results are shown in the following sections.

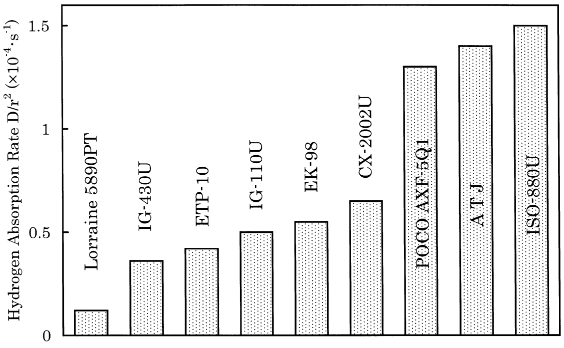

Fig. 1. Hydrogen absorption rates into graphites and a CFC at 1273 K under a hydrogen pressure of 10 kPa.

3.2. Pressure dependence of hydrogen absorption

Fig. 2 shows the pressure dependence of hydrogen retention measured for IG-110U at 1273 K. The authors have reported that hydrogen retention obeys Sieverts' law and is proportional to the square root of hydrogen pressure [4], however, it appears to deviate from the law above 10 kPa, although the behavior has already been assumed in [6].

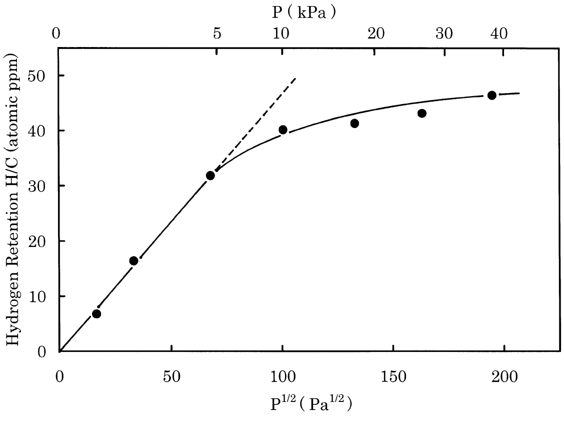

Fig. 2. Pressure dependence of bulk hydrogen retention in IG-110U graphite exposed to hydrogen gas at 1273 K.

Absorption rate constants are shown in Fig. 3. A variation between the low and high pressure range is clearly visible. It could be suggested that a trapping strongly influences the absorption process. Namely, for low concentration, the mobility of hydrogen will be suppressed by trapping, while for high concentration, hydrogen atoms can migrate since trapping sites have been already occupied. This suggestion is supported by the decrease of D/r^2 in neutron irradiated graphites with 50 times more trapping sites, where the D/r^2 becomes 1.5–4% of unirradiated graphite. Moreover, such a trapping effect may result in differences between the inward migration rate (absorption process) and the outward migration rate (desorption process), which was already suggested in [4]. In the process of inward migration, hydrogen atoms can be continuously supplied. In the case of outward migration, on the other hand, hydrogen atoms, which are not trapped and/or are weakly trapped, can be readily released, while, strongly trapped hydrogen cannot migrate, leading to a low diffusion coefficient and a high activation energy for diffusion. These arguments are consistent with the model, where two kinds of trapping sites would exist in graphite [19,20].

3.3. Oxidation and oxygen impurity effect

Hydrogen retention and absorption rate constants in oxidized graphite are shown in Fig. 4. The weight loss after oxidation at 973 K for 2 h was 1.3%, and it was 5.4% for 1073 K. Prior to hydrogen absorption measurements, vacuum outgassing was performed. The outgassing temperature influences the hydrogen retention and absorption rates. Although release of CO and CO_2 from graphite has a maximum at around 773–873 K, it tends to increase above 1273 K [21]. Hence, oxygen impurity atoms should still exist in the sample. However, the hydrogen retention after outgassing in the range of 1273–1673 K is smaller than that in the unoxidized sample. This suggests that oxygen impurities in graphite do not interact with hydrogen atoms. The hydrogen retention after outgassing at 1773 K shows a higher value than that of the unoxidized sample. Oxygen attack on graphite may produce new trapping sites.

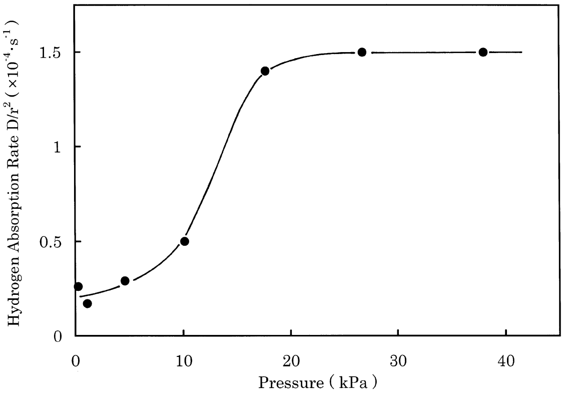

Fig. 3. Changes in hydrogen absorption rates into IG-110U graphite exposed at 1273 K as a function of hydrogen pressure (lines are guide to the eyes).

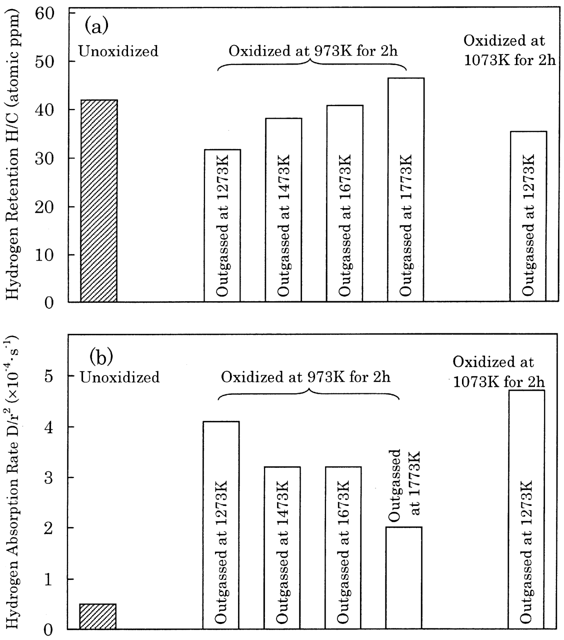

Fig. 4. Hydrogen bulk retention and absorption rate constants of IG-110U graphite previously oxidized at 973 and 1073 K. Hydrogen absorption was measured at 1273 K under a pressure of 10 kPa. Outgassing at various temperatures was performed prior to each measurement.

A significant increase up to eight times was observed in the hydrogen absorption rate for oxidized samples (Fig. 4(b)). However, when a higher outgassing temperature was applied, D/r^2 showed a tendency to decrease toward the value of the unoxidized sample. This phenomenon also suggests oxygen impurities do not trap hydrogen atoms. The enhancement of the apparent diffusion rate may be explained by one of the following reasons: (1) diffusion paths were changed by oxidation, (2) original trapping sites were extinguished (or burned out) and (3) trapping sites became invisible due to occupation by oxygen atoms at the location of original trapping sites. It can be concluded from the reasons mentioned above that trapping sites for hydrogen may be located at a grain surface, near the grain surface region or on some boundaries in a grain, where oxygen atoms are accessible at 973 and 1073 K.

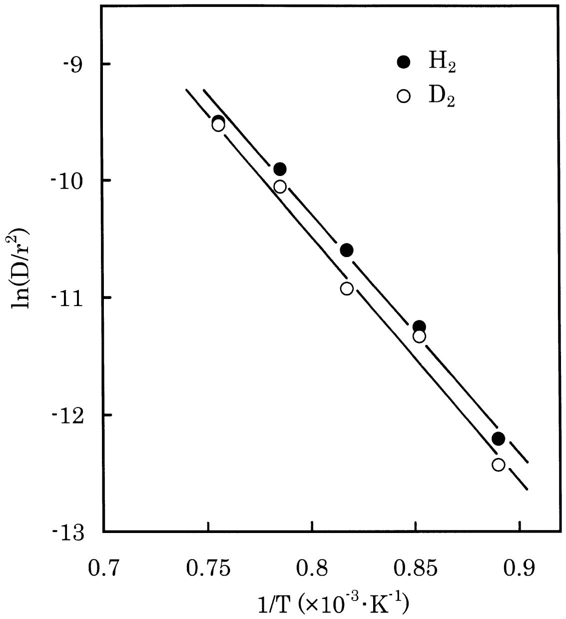

Fig. 5. Temperature dependence of hydrogen and deuterium absorption into IG-110U graphite under a pressure of 10 kPa.

3.4. Deuterium diffusion

Comparison of absorption rate constants of hydrogen and deuterium into graphite is shown in Fig. 5 for IG-110U. Diffusion of hydrogen, as expected, is faster than that of deuterium. The activation energies of hydrogen and deuterium diffusion in graphite can be estimated from the slopes as 153 and 158 kJ/mol, respectively. They are obviously smaller than the activation energies determined for the desorption process (e.g., 251 kJ/mol for deuterium [4] and 270 kJ/mol [22] for tritium).

4. Conclusions

The hydrogen bulk retention and absorption rates have been studied for various conditions. The results are summarized as follows:

1. Hydrogen absorption rates significantly differ with a variation of a factor 12 between the different brands of graphite and CFC. The difference can be ascribed to grain size, trap concentration, diffusion paths and an oxygen effect.
2. Hydrogen retention in IG-110U graphite obeyed Sieverts' law below 10 kPa, however, it tended to saturate above this pressure. It suggests the number of traps is not large in these samples.
3. Absorption rate constants differed 10 times between the case of low and high pressure. In the case of lower pressures, a small number of hydrogen atoms are easily subjected to trapping and this causes low mobility of hydrogen atoms.
4. Oxidation of graphite reduced hydrogen retention, and the impurity oxygen did not appear to behave as a hydrogen trap.
5. Hydrogen absorption rate in oxidized sample increases compared to unoxidized samples. This can be ascribed to the change of diffusion paths, reduction of trapping sites or occupation of oxygen atoms at the original trapping sites.
6. Activation energies for apparent diffusion process were estimated to be 153 and 158 kJ/mol for H_2 and D_2, respectively. These are considerably smaller than those determined from desorption measurements (250–270 kJ/mol). It may be a result of trapping.

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