Hydrogen retention in graphite and carbon materials under a fusion reactor environment

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Abstract

Bulk hydrogen retention and hydrogen diffusion in graphite and carbon materials have been studied to estimate hydrogen recycling and tritium inventory under a fusion reactor environment. Two kinds of hydrogen trapping sites may exist. The first will be one of lined carbon dangling bonds located at the edge surface of a crystallite with an adsorption enthalpy of 2.6 eV, the second will be a solitary carbon dangling bond, such as an interstitial cluster loop edge, with an enthalpy of 4.4 eV. The correlation between hydrogen retention and the microstructure should refer to the edge surface area of a crystallite for an unirradiated sample and to lattice spacing along the *c* axis for an irradiated sample. The diffusion process is the rate-determining step for hydrogen absorption into graphite, and detrapping dominates the hydrogen desorption process due to the high trapping energy.
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1. Introduction

Graphite and carbon materials are two of the best candidates as plasma facing components in next generation fusion experimental reactors [1,2]. However, carbon materials raise the hydrogen recycling rate and the tritium inventory due to their affinity to hydrogen. Hydrogen recycling is a critical issue for such reactors which aim to realize long pulse or steady state operation. Since hydrogen can move deep into graphite material, bulk hydrogen retention seems to dominate the hydrogen retention at temperatures above 1000 K [3], while hydrogen implanted within the subsurface regions would be released at a lower temperature. In order to estimate the hydrogen recycling and tritium inventory in graphite and carbon materials at such high temperatures, it is necessary to clarify the hydrogen trapping and transport

mechanism in the material. Numerous studies have been performed on graphite exposed to hydrogen gas [4–17]. However, fundamental information about hydrogen behavior in carbon has not been well-defined. The amount of hydrogen retained depends on the maker and brand of graphite [9,10], and the hydrogen diffusion coefficients also show a discrepancy of nearly five orders of magnitude. Furthermore, in a fusion reactor environment, neutron irradiation will enhance hydrogen retention in these materials [6,9,11,15,18]. Interpretation of the complicated behavior of hydrogen in graphite has begun [14,19], and the nature of hydrogen trapping is soon to be identified in a fusion reactor environment.

In the present study, bulk hydrogen retention and hydrogen diffusion in graphite and carbon materials have been investigated in order to estimate the hydrogen recycling and tritium inventory during operation of a fusion reactor. The key issues of the study are (1) correlation between hydrogen retention and the microstructure, (2) neutron irradiation effect on hydrogen retention and diffusion, and (3) modeling of hydrogen transport in carbon materials.

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2. Experimental

The samples used in this study were several brands of isotropic graphite such as IG-110U, IG-430U, ISO-880U (Toyo Tanso Co. Ltd.) and CFC materials such as CX-2002U (Toyo Tanso Co. Ltd.) and PCC-2S (Hitachi Chemical Co. Ltd.) (all specimens are described in [10,13]). The samples used in each measurement were approximately 6 g (sheets of $5 \times 33 \times 1$ mm^3), although the dimensions of the samples influenced neither hydrogen retention nor the absorption rate. Prior to hydrogen gas exposure, the samples were annealed at a given temperature of 1773 K for 1 h in a vacuum to desorb the occluding gas. Hydrogen retention and absorption rates were evaluated with the method described in [9] by a pressure decrease in a constant volume system with a Baratron capacitance manometer (390H, MKS Inc.) until the equilibrium state was established (elapsed time: 0.5–30 h). The temperature of the system was controlled with an accuracy of ± 0.1 K, and the fluctuation of pressure was below 0.05%. The pressure range of the experiments was 0.02–40 kPa. In order to reflect a fusion reactor environment some samples (IG-110U, IG-430U, ETP-10 and CX-2002U) were irradiated in the Japan Materials Testing Reactor (JMTR) at fluences of up to 6.0×10^{24} n/m^2 (>1 MeV) and at a temperature below 473 K to introduce defects in graphite materials.

3. Results and discussion

3.1. Hydrogen absorption and the trapping site

As mentioned in previous works [9,20], the pressure decrease due to hydrogen absorption into graphite and CFC samples can be apparently reproduced with a model of the diffusion-controlled process, but not with other processes such as a surface reaction. Fig. 1 shows a typical example of the results of hydrogen absorption experiments and the kinetic analysis. Theoretical pressure curves, shown in Fig. 1, were calculated to fit the experimental data with the assumption of an apparent diffusion coefficient, D, and solubility constant (the method is described in [9,20]). Theoretical curves exactly fit the experimental curves in the region where the absorption rate is fairly high, while, in the case of higher exposure pressure (>10 kPa), they deviate from the experimental curves in the region with depleted absorption rates (the latter part of each experiment), such as the example shown in Fig. 1(b). This suggests that there is another absorption process in addition to the major absorption process which previously could be analyzed with the diffusion-controlled process. The second process has a unique form of absorption, which starts at the time when the first step of absorption is about to terminate. Hydrogen absorption in graphite materials is
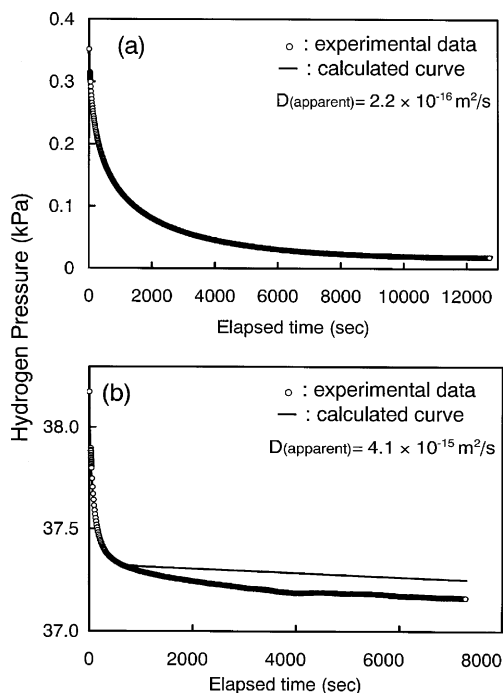

Fig. 1. Pressure change during hydrogen absorption experiments and the kinetic analysis as a diffusion-controlled process (sample: ISO-880U, exposure temperature: 1273 K). (a) initial pressure: 0.35 kPa, (b) initial pressure: 38.2 kPa.

attributable to the trapping of hydrogen atoms at the edge surface of a crystallite at the energy level of 2.6 eV [21,22]. On the other hand, Kanashenko et al. [14] and Chernikov et al. [19] have suggested another high-energy trapping site (4.4 eV) at the edge of a submicroscopic interstitial cluster inside the crystallite. Since a trapping site at the edge surface would produce an equilibrium state of trapping and detrapping for hydrogen atoms supplied continuously from outside the sample [10,22], hydrogen atoms can not penetrate into a crystallite if the trapping sites are not almost completely occupied by hydrogen atoms. This corresponds well with the property of the second absorption process, which starts nearly at the end of the first process, since a sufficient number of hydrogen atoms does not reach the surface of a crystallite at the initial stage of absorption. This could also explain why the second absorption process was observed at higher exposure pressures and not at lower pressures. Here, in accordance to the definition by Kanashenko et al. [14], the high-energy trap located at an interstitial cluster is named as Trap 1 (adsorption enthalpy: 4.4 eV), and the low-energy trapping site at the edge surface is named Trap 2 (adsorption enthalpy: 2.3 eV by Kanashenko et al. [14] and 2.6 eV by Atsumi [21,22]).
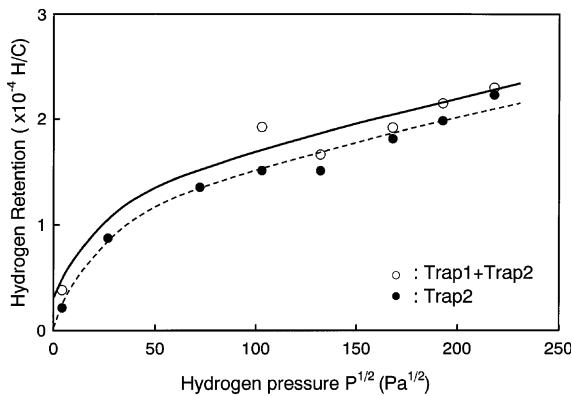
Fig. 2. Pressure dependence of bulk hydrogen retention corresponding to Traps 1 and 2 in ISO-880U graphite exposed to hydrogen gas at 1273 K.

The amount of absorbed hydrogen into Traps 1 was estimated from the difference between the experimental pressure decrease and the corresponding theoretical curve. Pressure dependence on the estimated hydrogen retention is given in Fig. 2 distinct for Traps 1 and 2. In some data for lower pressures (<10 kPa), the retentions cannot be estimated well, since the second absorption process was not clearly observed. One can conclude from Fig. 1 that the retention in Traps 1 is much smaller than that of Traps 2, and it appears to be a constant value without any pressure dependency, while Kanashenko et al. [14] have suggested that a pressure dependency does exist for Traps 1.

The pressure decrease in the absorption by Traps 1 was found not to fit with the curve of the diffusion-controlled process, which shows a drastic decrease at an initial stage of absorption like those shown in Fig. 1(a) and (b), but to fit well with a simple exponential function. The rate-determining step of this absorption would be (1) surface dissociation, (2) detrapping from Trap 2 or (3) intercalate atomic diffusion within a crystallite. Since the curve of pressure decreases simply obeying an exponential function (Fig. 1(b)), it suggests the absorption process is not diffusion-controlled. Although the shape of the curve does not fit well, apparent diffusion coefficients were tentatively determined. The resulting values of diffusion coefficients are 10 times smaller than those reported by Morita et al. [23] and Tanabe and Watanabe [24] as intercalate atomic diffusion, and also the activation energy of diffusion is larger by roughly 5 times (close to the detrapping energy from the edge surface [21,22]). For the above reasons, absorption should not be ascribed to intercalate atomic diffusion. Since both of the reactions of surface dissociation and detrapping are a first-ordered reaction, the change of the reaction rate derived from a pressure decrease was investigated at various temperatures. The activation

energy of the reaction which controlled the hydrogen absorption could be estimated to be 1.25 eV from the temperature dependence of measured reaction rates. This value is considerably smaller than that of detrapping energy from Trap 2 (2.6 eV) [21,22], and corresponds well with the activation energy of crystallite boundary diffusion (1.3 eV) [21] which controls the absorption process by Traps 2. In previous works [21,22], the chemical form of hydrogen may be molecular for the crystallite boundary diffusion, since a distinct energy peak would not appear at the grain surface. However, the energy seems too high if a hydrogen molecule migrates between crystallites without changing chemical form, since molecular diffusion of hydrogen usually shows small activation energies (e.g. 0.46 eV in SiO_2 [25]). In the diffusion process, hydrogen species might migrate, for instance, in a sequence of dissociation and recombination resulting from an interaction with the outer surface of a crystallite to derive the activation energy. Hence, the hydrogen transport from an edge surface to the inside of a crystallite would be controlled by dissociation (~1.3 eV) without any high or distinct energy barriers.

3.2. Mechanisms of hydrogen transport in a graphite material

Bulk hydrogen retention in graphites and CFCs differs significantly among different brands [10], and it becomes up to 50 times larger after neutron irradiation [9]. The author explained the cause as being due to the number of defects in the graphite structure [10]. According to this theory, the degree of graphitization (crystalline perfection) is strongly correlated with the hydrogen retention. The degrees of graphitization were estimated from the lattice constant, c_0, applying the model by Franklin [26], where interstitial carbon atoms expand the distance between graphite intercalations. This seems to have succeeded in reproducing the hydrogen retention phenomena, however, this model was corrected for correlation with crystallite size through the discussion of the location of trapping sites [13]. These two models are given in Fig. 3. The edge surface area was estimated from the dimensions of crystallites, which were defined by the width of Bragg peaks appearing in the X-ray diffraction pattern. For the estimation of the edge surface, it was assumed that the entire edge plane does not bind with atoms, however, in practice, the area is increased by the bond between each crystallite. In case of unirradiated samples, hydrogen retention in graphites and CFCs shows fairly good correlation with the edge surface area (Fig. 3(b) and [22]). Although neutron irradiation decreases the size of crystallites and leads to an increased edge surface area, hydrogen retention shows much larger values. According to the model mentioned in the last section, the correlation between hydrogen
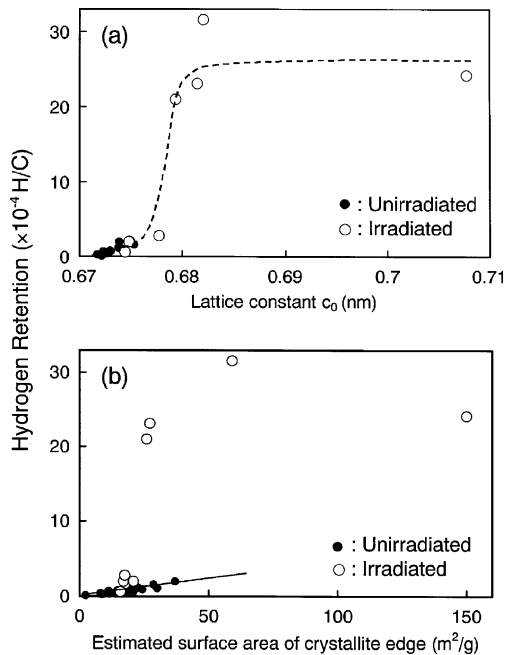
Fig. 3. Correlation of the hydrogen retention in graphites and CFCs with the lattice constant c_0 (a) and the edge surface area (b) (exposure temperature: 1273K, equilibrium hydrogen pressure: 10 kPa).

Fig. 4. Schematic illustration of the proposed model on hydrogen trapping and transport in a graphite material.

retention and the edge surface area corresponds to the trapping of hydrogen at Traps 2. This correlation is realized when the number of Traps 1 (radiation induced defects) is small, namely, in the case of an unirradiated sample (Fig. 2). Since a large number of Traps 1 will be produced by neutron irradiation, the correlation with edge surface area cannot be applied for irradiated samples. Either the interstitial loops or zigzag transformation produced by neutron irradiation expands the lattice spacing along the direction of c axis, the correlation for irradiated samples should be considered in relation to the lattice constant, c_0 (Fig. 3(a)). If these hypotheses are correct, the number of Trap 1 in irradiated samples can be estimated from the difference in the total hydrogen retention and the value derived from the line drawn in Fig. 3(b).

Based on the results obtained in this work, a hydrogen transport model in graphite materials has been devised. Fig. 4 shows a schematic illustration of the model. In an absorption experiment, a hydrogen molecule can easily reach the surface of a filler grain. Then, hydrogen will migrate into the filler grain apparently as molecule (in practice, it might be a sequence of dissociation and recombination), controlled by the diffusion process with an activation energy of 1.3 eV (the transport can be regarded as a molecular diffusion in the case of a s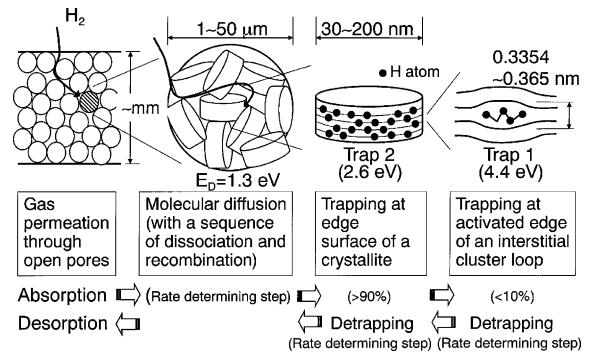equence of reactions in contrast to a reaction at a specific place). The hydrogen will be trapped at edge surfaces of crystallites by a covalent bond with the adsorption enthalpy of 2.6 eV. There are interstitial cluster loops or zigzag structures inside a crystallite, and high-energy trapping sites (4.4 eV) of solitary dangling bonds seem to be present at the edge of the cluster loops or zigzag structures [22]. In the case of unirradiated samples, the number of Trap 1 sites would be below 10% of the total number of trapping sites. Since high-energy sites will trap all of the approaching hydrogen atoms, it has no pressure dependency. As mentioned above, in absorption experiments, the hydrogen absorption process should be controlled by diffusion, where a hydrogen molecule is sent to Traps 2. On the other hand, the desorption process should be controlled by detrapping from Traps 1 or 2, due to a higher energy of trapping (2.6 eV or 4.4 eV) than the activation energy of diffusion. In fact, activation energies of the absorption process were estimated to be 1.3 eV [21], and in desorption process, they are 2.6 eV (unirradiated sample) or 3.3–4.3 eV (irradiated sample), where the Trap 2 is the major sites for unirradiated samples and the number of Trap 1 is much higher in irradiated samples.

4. Conclusions

Bulk hydrogen retention and the mechanisms of hydrogen transport in graphite and carbon materials have been examined. The results obtained in the present study are summarized as follows:

(1) Two kinds of trapping sites exist as the cause of bulk hydrogen retention. One will be a carbon dangling bond located at the edge surface of a crystallite with the adsorption enthalpy of 2.6 eV (Trap 2), and the other will be an interstitial cluster loop edge or a solitary dangling bond at a zigzag edge inside a crystallite with the energy of 4.4 eV (Trap 1). Hydrogen retention for Traps 2 has a pressure dependence due

to the equilibrium of trapping and detrapping according to the ambient pressure, on the other hand Traps 1 do not, due to the high energy of adsorption.

(2) The major sites are Traps 1 in an irradiated sample and Traps 2 in an unirradiated sample. Therefore, the correlation between hydrogen retention and the microstructure should refer to the edge surface area of crystallite for an unirradiated sample and to a lattice constant, c_0, for an irradiated sample.

(3) Within the discussed model of the absorption experiment, the absorption rate is controlled by a diffusion process, where a hydrogen molecule is sent to Traps 2, on the other hand, the desorption rate is controlled by detrapping process from Traps 1 and 2, due to their high energies of adsorption.

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