Hydrogen absorption and transport in graphite materials

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Abstract

Hydrogen absorption and transport in graphite materials have been studied to obtain fundamental information for a fusion reactor application and for hydrogen storage materials. Two kinds of hydrogen trapping sites should exist. One will be carbon dangling bonds located at the edge surface of a crystallite with an adsorption enthalpy of 2.6 eV, the other will be a solitary carbon dangling bond introduced by ion or neutron irradiation, such as an interstitial cluster loop edge, with an enthalpy of 4.4 eV. The results are compared with thermal desorption spectra of deuterium from graphites which were gas charged, ion irradiated and nano-structured by ball milling. These spectra can be well represented with three kinds of desorption process with activation energies of 1.3, 2.6 and 4.4 eV.
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1. Introduction

Graphite and carbon materials are attractive candidates for plasma facing components in current and future thermonuclear fusion devices [1,2]. From the viewpoint of plasma density control and reducing tritium inventory, various studies have been intensively performed on hydrogen behavior in these materials [3,4]. Fundamental information about hydrogen behavior in carbon and graphite has not been defined yet. The amount of hydrogen retained depends on the maker and brand of graphite [5,6], and the hydrogen diffusion coefficients also show a discrepancy of nearly five orders of magnitude [4,5].

On the other hand, these materials, especially with nano-structure such as carbon nanotubes [7,8], graphitic nanofibers [9] and mechanically milled graphite [10], have recently took a great deal of attention as hydrogen storage materials, although some data on carbon nanotubes and graphitic nanofibers seem to be taken as doubtful [11,12]. However, the mechanisms of hydrogen adsorption and the nature of the chemical interaction have not sufficiently been clarified. To obtain such information is quite im-

portant in order to improve hydrogen storage capacity and control the absorption/desorption rate.

In the present study, the chemical form of hydrogen in graphite materials and the transport process have been investigated.

2. Experimental

The specimens used in this study were several brands of isotropic graphite such as IG-110U, ISO-88 and ISO-880U (the purified material of ISO-88) manufactured by Toyo Tanso. Following three experiments were performed: (1) hydrogen absorption experiments, (2) ion implantation experiments and (3) thermal desorption spectroscopy (TDS). Prior to introduce hydrogen, the specimens were annealed at given temperatures of 1773 and 1673 K for experiments (1) and (2), respectively. Hydrogen absorption would not take place when this outgassing is insufficient [13]. In hydrogen absorption experiments, hydrogen retention (the amount of absorption) and absorption rates were evaluated with the method described in Refs. [5,14,15] by a pressure decrease in a constant volume system with a Baratron capacitance manometer (390H, MKS) 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

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of pressure was below 0.05%. The pressure range of the experiments was 0.02–40 kPa. Ion irradiation was performed with 20 keV D_2^+ ions at normal incidence and at ambient temperature. Current density was kept up to 5 A/m^2 during irradiation. Total ion doses ranged from 5.0×10^{20} to 5.0×10^{22} ions/m^2. TDS measurements were carried out with a constant heating rate of 10 K/min in a vacuum below 10^{-6} Pa. Hydrogen used for TDS experiments was its isotope, or deuterium, to advance sensitivity. Released species were analyzed with a quadrupole mass spectrometer (MSQ-300, Ulvac).

3. Results and discussion

3.1. Hydrogen absorption

Graphite and carbon fiber/carbon composites (CFCs) absorb hydrogen to the concentration of 20–600 ppm under 0.1 MPa of hydrogen gas, depending on the maker and brand [5,6]. Hydrogen retention in graphites and CFCs (including neutron or ion irradiated samples) shows good correlation with the lattice constant, c_0, which reflects the degree of graphitization, or crystalline perfection [6,16]. However, in the case of unirradiated samples, there is better correlation with the edge surface area which was estimated from the dimensions of crystallites defined by the width of Bragg peaks appearing in the X-ray diffraction pattern [16,17].

The pressure decrease due to hydrogen absorption into graphite materials seems to be controlled by the diffusion process, but not by other processes such as a surface reaction. Typical examples are shown in Fig. 1 with kinetic analysis. Theoretical pressure curves can be calculated to fit the experimental data with the assumption of an apparent diffusion coefficient, D, and a solubility constant (the method is described in Refs. [5,14,15]). Theoretical curves exactly fit the experimental curves in the region where the absorption rate is rather high, while, in the case of higher exposure pressure (>10 kPa), they show discrepancy with the experimental curves in the region where hydrogen absorption is about to terminate (e.g., Fig. 1b). This suggests that there is another absorption process in addition to the major absorption process. The second process shows a unique feature of absorption, which starts at the time when the first process of absorption is about to be completed. In previous reports [16,17], it has been shown that the major portion of hydrogen absorption (the first process) is attributable to the trapping at the edge surface of crystallites. The second absorption process, therefore, is attributable to the permeation of hydrogen into the inside of a crystallite. The amount of hydrogen retention has a dependency nearly of the square root of pressure (Fig. 2), and this can be explained well with an equilibrium reaction between hydrogen molecules and the trapping sites [6]. Hence, in the case of the initial stage of
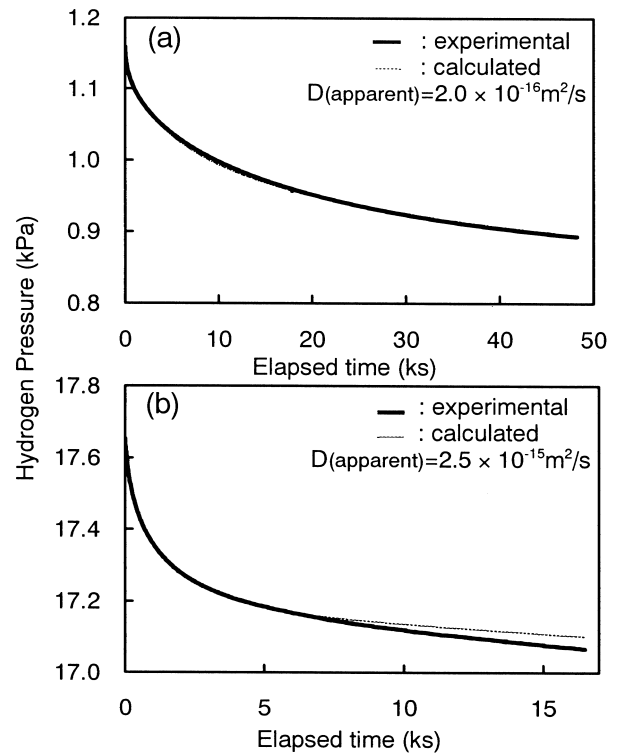

Fig. 1. Pressure change during hydrogen absorption experiments and the kinetic analysis as a diffusion-controlled process (sample, IG-110U; exposure temperature, 1273 K). (a) Initial pressure, 1.15 kPa; (b) initial pressure, 17.64 kPa.

hydrogen absorption and the absorption under a low hydrogen pressure, the trapping sites located at the edge surface will behave as a barrier against the permeation of hydrogen into the inside of a crystallite, since the occupation of trapping sites is not sufficient. It agrees well the experimental results, where the second process started near the termination of the first absorption process and the second process was observed only at a high hydrogen pressure.

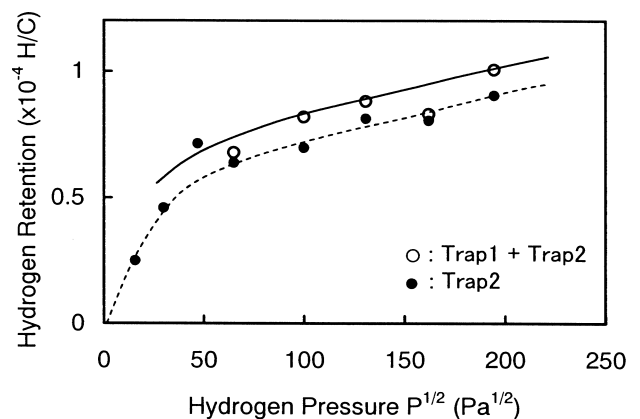Kanashenko et al. [18] have proposed two kinds of

Fig. 2. Pressure dependence of bulk hydrogen retention corresponding to Traps 1 and 2 in IG-110U graphite exposed to hydrogen gas at 1273 K.

trapping sites for hydrogen in graphite. Although both trapping sites are carbon dangling bonds, one is the high-energy trapping site named as Traps 1 located at an interstitial cluster, and the other is the low-energy trapping site named as Traps 2 at the edge surface, in accordance to their definition. The adsorption enthalpies seem to be 4.4 and 2.3 eV, respectively. The enthalpy of 4.4 eV was derived from the difference between C–H bond strength in a hydrocarbon molecule (4.45 eV$\times$2) and the dissociation energy of an H_2 molecule (4.5 eV). If carbon dangling bonds exist side by side (it is plausible at the ordinary edge surface), they would interact with each other forming a relaxed state. The relaxation energy quoted was ~1 eV/ atom (calculated by quantum-mechanical method [19]). Then the adsorption enthalpy is subject to reduction of 1.9 to be 2.3 eV. For the above reasons, Traps 1 may be solitary carbon dangling bonds existing in an intercalation of graphite structure. It is highly suggestive that both activation energies of deuterium desorption are 2.6 eV from gas charged graphite [20] and ion implanted graphite (peak II) [21,22]. Since the trapping site of hydrogen for gas charged graphite has been deduced to be a carbon dangling bond located at the edge surface of a filler grain [17], the site should correspond to Traps 2. The discrepancy of 2.3 and 2.6 eV may be caused by the estimation of the relaxation energy. In this study, the value of 2.6 eV has been applied as the enthalpy of Traps 2 in accordance with experimental results. The concept of Traps 1 is also consistent with the present results, where the site may exist in a crystallite. The second absorption process observed in the present study can be ascribed to the hydrogen trapping to Traps 1. The amount of absorbed hydrogen into Traps 1 can be estimated from the difference between the experimental pressure decrease and the corresponding theoretical curve. Fig. 2 shows pressure dependence on the estimated hydrogen retention corresponding to Traps 1 and 2. One can conclude that the retention in Traps 2 dominates the total hydrogen retention in graphite. And a pressure dependency can be observed only for Traps 2, while it appears to be constant for Traps 1. Taking account of the high energy of Traps 1, this may be caused by one-sided trapping without making a visible equilibrium state at such a temperature range below 1300 K.

Based on the results discussed in this study, a schematic view of the proposed model on hydrogen trapping in graphite materials is given in Fig. 3. In a hydrogen absorption process, hydrogen molecules permeate into graphite through the boundary of filler grains, or open pores. In the filler grains, there are crystallites of 30–200 nm. Hydrogen is transported thorough the boundaries of crystallites in the form of a molecule (precisely, it may be the sequence of dissociation and recombination) with an activation energy of 1.3 eV [13,23]. Then the hydrogen molecules will be dissociated to bind with carbon dangling bonds at the edge surface (Traps 2). If Traps 2 are sufficiently occupied, hydrogen atoms can permeate into a
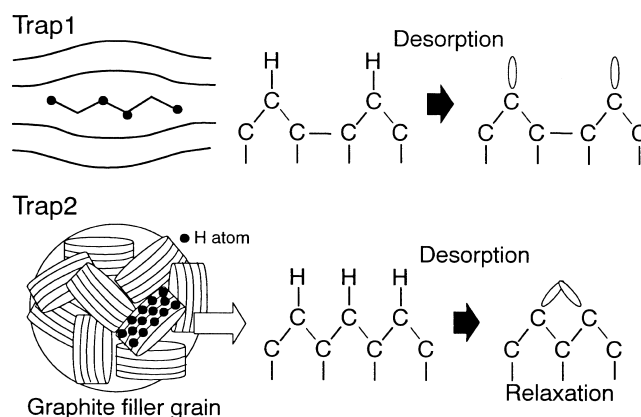

Fig. 3. Schematic illustration of the proposed model on hydrogen trapping in a graphite material. The chemical bond model was referred from Ref. [18].

crystallite to be caught by Traps 1. Traps 1 make C–H bonds which do not show a relaxed state after dissociation. It has been believed that interstitial loops are produced in graphite intercalations by ion or neutron irradiation [24,25], and recent reports [26,27] also support this theory. On the other hand, a new model has recently been introduced [28], where irradiation (including electron) makes sp^3 chemical bonds and non-6-fold atomic rings, and some authors support this interpretation [29,30]. Such damaged structures possibly have solitary carbon dangling bonds in graphite intercalations, while there must be linearly arranged dangling bonds at the edge surface of a crystallite. If there are such solitary bonds, it realizes high-energy traps for hydrogen in graphite materials.

3.2. Hydrogen transport and desorption

On the basis of the above discussion, a comparison of theoretical simulation with various experimental results on TDS measurements has been tested. The results are shown in Fig. 4. Two data (Fig. 4a,b) were obtained by the author, where Fig. 4a was previously published [20], and the other data (Fig. 4c) were measured on mechanically milled graphite reported by Orimo et al. [10]. Although the desorption rates are normalized, the total amounts of retained deuterium (D/C) were quite different to be approximately 0.0003, 0.3 and 0.95 for the data shown in Fig. 4a–c, respectively. The TDS spectrum from gas charged isotropic graphite (Fig. 4a) shows two peaks at 735 and 1220 K, and it can be well interpreted with a diffusion-controlled process. Precisely, the fundamental processes of the desorption for both peaks would be recombination; however, due to the long path to the surface, hydrogen will be subjected to a sequence of trapping and detrapping. This will result in an apparent diffusion for the dominant process of desorption. TDS spectra from hydrogen ion implanted graphite are believed to have three peaks [21,22]. However, it seems to be two
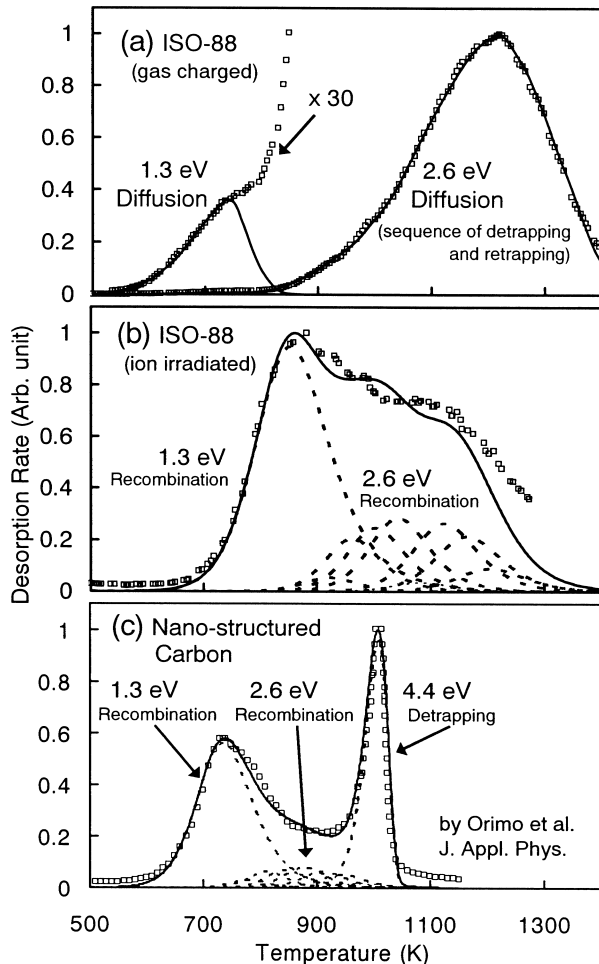
Fig. 4. Deuterium desorption spectra and the curve fittings for (a) gas charged graphite (ISO-88, hydrogen charged at 973 K at 60 kPa for 5 h) [20], (b) ion implanted graphite (ISO-88, 20 keV D_2^+ to a dose of 5.0×10^{22} ions/m^2) and (c) nano-structured carbon milled in hydrogen atmosphere [10]. The heating rate in all experiments was 10 K/min. The open squares are experimental data, and the solid curves are calculated data.

peaks (Fig. 4b) and, in some cases, to be one [31], depending on the conditions such as the ion energy, dose, temperature and heating rate. The graphite structure will be distorted with the duration of irradiation. Then, the enthalpy of 2.6 eV should change and has a wide distribution due to the change of the relaxation energy. Such an interpretation assuming a distribution of activation energy has been actually performed on the TDS spectra from graphite implanted with hydrogen ions [32], since the TDS spectra are considerably broader than those of theoretical curves with the corresponding activation energy. This simulation has also been applied in this study (Fig. 4b). The desorption which has an activation energy of 1.3 eV is assumed to be a recombination-controlled process due to the shorter path compared with gas charged graphite. This interpretation well represents the experimental TDS spectra. The peak corresponding to 4.4 eV could not be identified, and this may be buried in the spectra or exist at

much higher temperature region. Hydrogen desorption with an energy of 4.4 eV can be observed in Fig. 4c. The milled graphite would be much atomized to have a very short path for desorption, hence, it will not be ascribed to the apparent diffusion process. Since disordering or distortion should be introduced in graphite structure during the milling process, the curve fitting fairly represents the TDS result.

4. Conclusions

Hydrogen absorption and transport in graphite materials have been examined. The results obtained in the present study are summarized as follows:

(1) There are two kinds of trapping sites for hydrogen in graphite materials. One will be an interstitial cluster loop edge or a solitary dangling bond located in a crystallite with the energy of 4.4 eV (Traps 1), the other is a carbon dangling bond located at the edge surface of a crystallite with the adsorption enthalpy of 2.6 eV (Traps 2). Traps 2 dominate hydrogen retention in a usual graphite sample. Hydrogen retention for Traps 2 has pressure dependence due to the equilibrium of trapping and detrapping, on the other hand, Traps 1 do not, due to the high energy of adsorption.
(2) In the case of ion or neutron irradiated graphite, the adsorption enthalpy of 2.6 eV shows an energy distribution due to the lattice disordering or lattice distortion, since the enthalpy relates with the relaxation process.
(3) Thermal desorption spectra of deuterium released from gas charged graphite, ion implanted graphite and mechanically milled graphite were simulated with desorption processes with activation energies of 1.3, 2.6 and 4.4 eV. Theoretical desorption curves can fairly represent these TDS spectra.

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