Retention and release of hydrogen isotopes in carbon materials priorly charged in gas phase

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ABSTRACT

Thermal desorption of deuterium from isotropic graphites and a CFC material priorly charged with deuterium gas has been investigated to obtain quantitative information on hydrogen recycling and tritium inventory in fusion experimental devices and future reactors. The spectra of thermal desorption spectrometry (TDS) appear to have five peaks, which are defined as peaks 1–5 in order of the increase of temperature. Diffusion coefficients of deuterium for the absorption process are evaluated for the samples charged with deuterium gas for various absorption times. Absorption pressure dependence of TDS spectra shows a unique change in the temperatures of peak 2. As for the absorption temperature dependence of TDS spectra, peak 4 has a drastic change in the shape of spectra and also in the peak temperatures. The mechanism of desorption for peak 5 will be associated to a detrapping process with a dispersion of energies in the range of 4.0–4.9 eV.

1. Introduction

Graphite and carbon materials have been used for plasma facing materials in various major-scale fusion devices to produce high density and high temperature plasmas [1]. However, they have disadvantages in a high tritium inventory, high erosion yield and neutron-induced degradation of thermal conductivity [2,3]. Nevertheless they still may be the ideal material for divertor plates, if the divertor heat load cannot be lowered, where the disadvantages will be moderated [4].

Although there are numerous data measured for hydrogen in carbon and graphite, hydrogen behavior are considerably different depending on the kind of samples and the experimental conditions, and furthermore, the interpretations of the behaviors are quite diverse [5–16]. A technique of gas charge, employed in the present study, is a unique method to obtain information on hydrogen behavior and kinetic parameters without producing additional defects and changing any structures of graphite and carbon.

In the present study, experiments on thermal desorption spectrometry (TDS) were carried out to obtain thermodynamic and kinetic information of hydrogen behavior in graphite with changing parameters of deuterium gas charge before a TDS measurement.

2. Experimental

The samples mainly used in this study were isotropic graphite (ISO-880U, Toyo Tanso Ltd.). ISO-880U is an ultra-high purity grade of ISO-88 consisting of fine grain particles of ca. 5 μm, which was designed for low porosity and high mechanical strength type graphite. These samples were outgassed at 1720 K for 2 h below 10^{-3} Pa prior to gas charge. The gas charging was carried out in D_2 gas within a pressure range of 0.8–64 kPa at a temperature range of 973–1323 K for a given absorption time within 0.06–360 ks. After the gas charge, the samples were quenched within 30 s to a room temperature to preserve the state of the high temperature. TDS spectra released from the gas-charged samples were measured up to 1735 K basically at a constant heating rate of 0.1 K/s in a vacuum below 10^{-5} Pa with a quadrupole mass spectrometer (BGM-102, ULVAC Ltd.). The determined species of TDS experiments were H_2, HD, D_2, CHD_3, CD_4, HDO, D_2O, etc., In the following results and discussion section, only the results for D_2 desorption are mentioned, since the desorption of hydrocarbon is significantly smaller than that of D_2.

3. Results and discussion

3.1. Thermal desorption spectrometry (TDS)

The authors have previously determined TDS spectra for 29 brands of graphite and carbon materials such as isotropic graphite, highly oriented pyrolytic graphite (HOPG), carbon fiber carbon composites (CFCs) and glassy carbon [15]. Typical results on these materials are
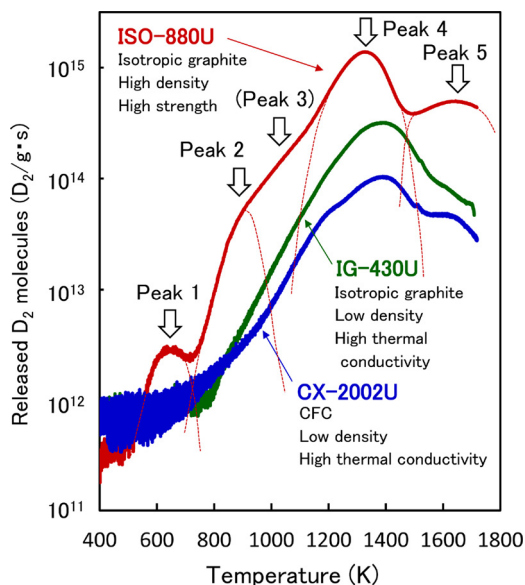

Fig. 1. Typical TDS spectra of deuterium release from isotropic graphites and a CFC (absorption temperature: 1273 K, D_2 pressure: 42 kPa, absorption time 8–30 h, heating ramp rate of TDS: 6 K/min). Dashed lines are added for better visibility.

given in Fig. 1. High density and high strength type graphites (e.g. ISO-880U: 1.90 g/cm³, 69 MPa (tensile strength)) show large amounts of deuterium desorption, which reflects a low degree of graphitization and their small size of crystallite [17,18]. They appear to have five desorption peaks, although peak 2 appears to be a shoulder, and peak 3 may not be distinct to be identified. Names of peaks from 1 to 5 are given in the order of temperatures. On the other hand, low density and high thermal conductive type graphites (e.g. IG-110U: 1.77 g/cm³, 120 W/m K and IG-430U: 1.82 g/cm³, 140 W/m K) show lower amounts of deuterium desorption, reflecting a high degree of graphitization. They do not accompany peak 1, which was associated to the molecular desorption of deuterium from closed pores [11,15]. They may not be enough dense to form isolated pores in the aggregation of graphite grains. As for CFCs (e.g. CX-2002U: 1.65 g/cm³, 280 W/m K), the TDS intensities are much smaller than those for isotropic graphites, which caused by a high degree of graphitization and their large size of crystallite on the contrary to isotropic graphites [17,18]. The background of mass number 4 scarcely existed even at 1735 K, and the deuterium release from these samples reached to the background level after sustaining the termination temperature of 1735 K for 3 h [15]. Actually, HOPG charged with deuterium gas shows almost no peaks in the TDS spectra and kept nearly the background of ion currents of the mass spectrometer [15].

3.2. Absorption time dependency on TDS

TDS spectra were investigated for ISO-880U charged with deuterium gas for various absorption times ranging from 1 min to 100 h. The results obtained are shown in Fig. 2. For the sample absorbed at 973 K, intensities of all the peaks increased with absorption times, and the temperatures of peaks 1, 4, and 5 are shifted to higher temperatures with the increase of absorption time (Fig. 2(a)). At higher absorption temperature of 1273 K, these phenomena can be observed only for peaks 4 and 5. Peak 3 for those two different absorption temperatures cannot be identified well. The temperature shifts for different absorption times suggest the absorption process corresponding to each peak should be controlled by deuterium diffusion into a medium, since an insufficient charge will produce a high concentration of deuterium around a surface region. Therefore, shorter absorption times should

lead the peak to shift toward lower temperatures. Curve fitting for experimental TDS spectra with calculated curves, which were assumed to be controlled by a diffusion process. The total amounts of released deuterium by integrating the corresponding curves were estimated. Fig. 3 shows the results of estimated amounts plotted against the square roots of absorption times. The diffusion coefficients can be derived from the fitting with experimental data. The results are compared with reported values in Fig. 4. As shown in Fig. 4, diffusion coefficients differ up to five orders of magnitude and activation energies are varied from 0.24 to 4.3 eV. These discrepancies should be caused by 1) the difference of experimental methods to determine these data whether from absorption or desorption, 2) the amount of objective hydrogen which influences to trapping effects, 3) irradiated materials or not, 4) difference of materials, such as isotropic graphite and HOPG. Details on individual data are explained in ref. [18]. Although the diffusing medium corresponding to peak 5, i.e. graphite filler grain or crystallite in a filler grain, cannot be ascertained at present, diffusion coefficients are not contradicted with reported values for hydrogen diffusion in unirradiated isotropic graphite measured for an absorption process.

3.3. Absorption pressure dependency on TDS

Absorption pressure dependency has already been reported by the authors [11]. The results are given in Fig. 5. Unique changes for each peak can be observed, even though the TDS spectra were measured for sufficiently charged samples to reach a saturated level. From discussion on the TDS data, peak 1 can be ascribed to the release of deuterium confined in closed pores in a D_2 molecular form. Peak 2 will originate from dissolved atoms as a solid solution in graphite, and they should be released by a recombination-controlled process. Peaks 3 and 4 are attributable to the release of deuterium from trapping sites located at a crystalline edge and an intercalate cluster, respectively. Details of the analysis should be referred in ref. [11].

3.4. Absorption temperature dependency on TDS

Fig. 6 shows TDS spectra of deuterium release from ISO-880U priorly charged with deuterium gas at various temperatures until saturation levels could be achieved for each sample. The differences in characteristics between the peaks can be explained as follows. First of all, peak 1 would not be influenced from a thermal equilibrium reaction, since deuterium molecules confined in closed pores do not have a chemical bond with carbon atoms. On the other hand, dissolved or trapped deuterium atoms corresponding to peaks 2, 3, and 4 with relatively small binding energies will be strongly affected by a thermal equilibrium reaction. If we assume the following reaction between a trapping site for deuterium ($-C^*$) and a deuterium molecule (D_2):

$$2 - C^* + D_2 \leftrightarrow 2 - C - D, \qquad (1)$$

the equilibrium constant of the reaction, k, can be expressed by

$$k = \frac{[-C-D]^2}{[-C^*]^2 \cdot P_{D2}}, \qquad (2)$$

where $[-C-D]$ and $[-C^*]$ are the concentration of occupied trapping sites and vacant trapping sites, respectively. And, P_{D2} is the equilibrium pressure of deuterium. Applying the following two equations:

$$\Delta G = \Delta H - T\Delta S, \qquad (3)$$

$$\Delta G = -RT \ln k, \qquad (4)$$

the occupation ratio of deuterium trapping sites, ε, can be derived as follows:

$$\varepsilon = \frac{[-C-D]}{[-C^*] + [-C-D]} \qquad (5)$$