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Bulk hydrogen retention in neutron-irradiated graphite at elevated temperatures

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ABSTRACT

Bulk hydrogen retention and the analysis of absorption kinetics have been studied on graphite samples irradiated with neutrons at various fluences. There are two kinds of hydrogen trapping sites: interstitial cluster loop edge sites (trap 1) and carbon dangling bonds at edge surfaces of a crystallite (trap 2). Neutron irradiation preferably creates trap 2 sites at lower fluences and trap 1 sites at higher fluences. The dissociation enthalpy becomes 2–3 times higher for neutron-irradiated samples due to the creation of high energy trapping sites. Absorption kinetics, such as diffusion coefficients and absorption rate constants are strongly affected by neutron irradiation and annealing after irradiation.

1. Introduction

Hydrogen recycling and tritium inventory are the critical issues for ITER and a next step fusion reactor which aims to realize long pulse or steady state operation. Graphite and CFCs, which are used for plasma facing walls or divertor plates in present fusion devices, raise the amount of hydrogen recycling and tritium inventory due to their affinity for hydrogen. Moreover, these carbon materials tend to show high erosion yields mainly caused by chemical sputtering. In particular, carbon materials with damaged structure, such as ion or neutron-irradiated samples and carbon dust, retain considerably high amounts of hydrogen [1–3]. For these reasons, carbon materials are employed only for a limited area of the divertor in ITER. However, there is still a possibility to use carbon materials at the whole first wall armors if the divertor surface is kept at a high temperature such as above 1000 K [4]. In that case, the hydrogen retention and tritium inventory would be dominated by bulk hydrogen retention and not by a saturated layer or a surface near region [5,6]. Hence, it is important to clarify the hydrogen behavior in bulk graphite especially having damaged structure.

The authors have studied the hydrogen absorption process into neutron-irradiated graphite focusing on the trapping site identification and on the increase of hydrogen retention [7,8]. In the present study, kinetic assessments on bulk hydrogen retention in neutron-irradiated graphite and its pre-annealing effects have been investigated.

2. Experimental

Attractive candidates for divertor plates of ITER and DEMO are CFCs, which consist of quite different components of fibers and matrices. However, for the first step to investigate the irradiation effects of hydrogen behavior, especially on kinetics, in graphite, materials with complicated structures may not competent for the test samples. Hence, three brands of isotropic graphite: IG-110U, IG-430U and ISO-880U (Toyo Tanso Co. Ltd.) were used for the specimens in this study. IG-110U is an ultra-high purity grade of IG-110, which is employed in High Temperature Engineering Test Reactor (HTTR) of JAEA as a moderator with high irradiation durability. IG-430U has been installed in JT-60U as high thermal conductive armor tiles (140 W/m K), and ISO-880U was designed for low porosity and high mechanical strength type graphite. They were irradiated in the Japan Materials Testing Reactor (JMTR) at fluences from 4.7×10^{22} n/m^2 to 5.4×10^{24} n/m^2 (>1 MeV) below 473 K. The damaged level has been estimated to be 0.006–0.65 dpa, respectively. These values are relevant to the estimated damage of 0.2–1.0 dpa for the first wall and divertor armor in ITER, which depend on the exchange lifetime of the components [9,10]. After neutron irradiation, hydrogen absorption into the sample at an elevated temperature ranged from 973 K to 1323 K, which was defined as an 'absorption temperature', was examined by placing the sample in a constant volume chamber backfilled with hydrogen gas. The gas pressure was monitored with Baratron capacitance manometers (390H and 627B, MKS Inc.). Hydrogen retention and absorption rates can be determined from the amount of pressure decrease and the change of decreasing rate, respectively. Absorption process, kinetically, can be explained well by diffusion-controlled process. However, since there are strong trapping sites for hydrogen atoms, diffusion process is suppressed

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by the trapping effects, such as 15 times smaller [11]. The apparent diffusion coefficients have been defined as a diffusion process including trapping effects [11,12], and they could be derived by fitting the pressure curve to a theoretically calculated curve [2].

3. Results and discussion

3.1. Hydrogen retention

The authors have ascertained that there are at least two kinds of trapping sites for hydrogen in graphite [11–14]. One is an interstitial cluster loop edge or a solitary carbon dangling bond located in intercalations with the energy of 4.4 eV (trap 1), and the other is a carbon dangling bond at the outside edge surface of a crystallite with the absorption enthalpy of 2.6 eV (trap 2) [13,14]. Hydrogen absorption into graphite takes place in two stages, since the sites exist at different places and the trap 2 behaves as a diffusion barrier for hydrogen penetration toward trap 1 until the trap 2 sites are fulfilled with hydrogen atoms. The first stage is the pressure decrease caused by absorption to trap 2, where the curve can be well expressed with a diffusion-controlled process. The second stage of absorption starts near the termination of the first stage, and the net pressure decrease of this stage obeys an exponential function, which means that the absorption process is controlled by a first-order reaction, such as dissociation of hydrogen molecules into atoms and detrapping of hydrogen atoms from trap 2. One can estimate the absorption rate constants from the hydrogen pressure decrease.

Hydrogen retention in graphite IG-430U as a function of neutron fluence is shown in Fig. 1. Both retentions corresponding to traps 1 and 2 significantly increase with the irradiation fluence. The total amount of hydrogen retained in the sample after irradiation at the highest fluence (0.65 dpa) is approximately 140 times higher than the one for an unirradiated sample. The retention for trap 2 is approximately 10 times larger than that for trap 1 at the initial stage of irradiation (0.047 and 0.094 dpa), while the ratio becomes smaller with increasing of irradiation fluences (3.0 for 0.14 dpa, and 2.1 for 0.39 dpa), and it finally reaches to be equal values (above 1.9 dpa). It shows that although the both retention for traps 1 and 2 increases with irradiation fluences, the increase for trap 2 takes place earlier and that for trap1 comes later. This delay can be ascribed to the nature of the sites, where the creation of interstitial cluster loops, namely traps 1, is necessary to accumulate point defects [15].

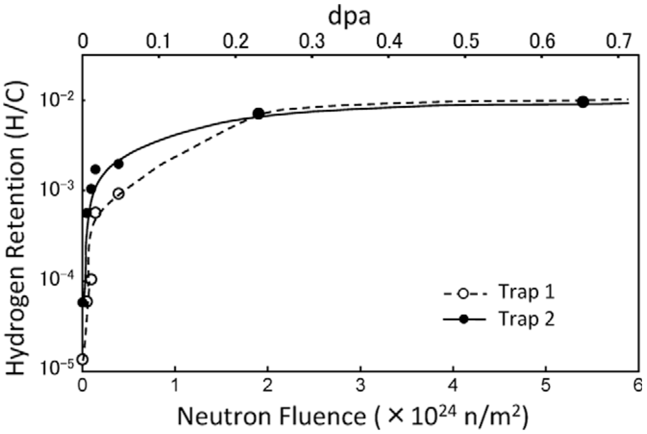

Fig. 1. Hydrogen retention in graphite irradiated with neutrons at various fluences corresponding to each trapping site. The lines are drawn to guide the eyes (sample: IG-430U, absorption temperature: 1273 K, equilibrium pressure: ∼10 kPa).

The temperature dependency of the hydrogen bulk retention in graphite samples is shown in Fig. 2. Enthalpies of hydrogen retention, or heat of solution, can be estimated from the slopes, and it could be observed that they have negative values. This indicates the hydrogen uptake occurs exothermically, and chemically stable bonds are formed in the sample. The enthalpies are 0.115 and 0.136 eV for unirradiated ISO-880U and IG-430U, respectively. And they increase by a factor of roughly 2–3 for neutron-irradiated samples, which are respectively 0.333 and 0.231 eV. It can be ascribed to the characters of the dominant trapping sites between unirradiated and irradiated samples. For unirradiated graphite, trap 2 with a lower binding energy is in overwhelming majority as a trapping site [7]. For an irradiated sample, on the other hand, hydrogen retention will be influenced by the increase of trap 1 with a high binding energy.

3.2. Absorption kinetics

Hydrogen diffusion coefficients obtained in this work are plotted in Fig. 3(a) as a function of neutron irradiation fluence. As mentioned before, since these values were estimated from the migration rate in a graphite filler grain, the diffusion of hydrogen should be strongly affected by trapping at trap 2 sites. These values, consequently, should be called 'apparent diffusion coefficients' as discussed elsewhere [11]. Practically, since the coefficient decreases by one fortieth at a neutron fluence of about 0.1 dpa, the hydrogen migration cannot be considered as the true diffusion process. In the figure, the diffusion coefficient decreases drastically even at lower fluences and it gradually increases with the irradiation fluence above −0.1 dpa. The increase may be ascribed to saturation of the concentration of trap 2 and a decrease of the size of diffusion medium, such as a reduction of the crystallite size [16] and a short circuit production caused by the incidence of micro cracks.

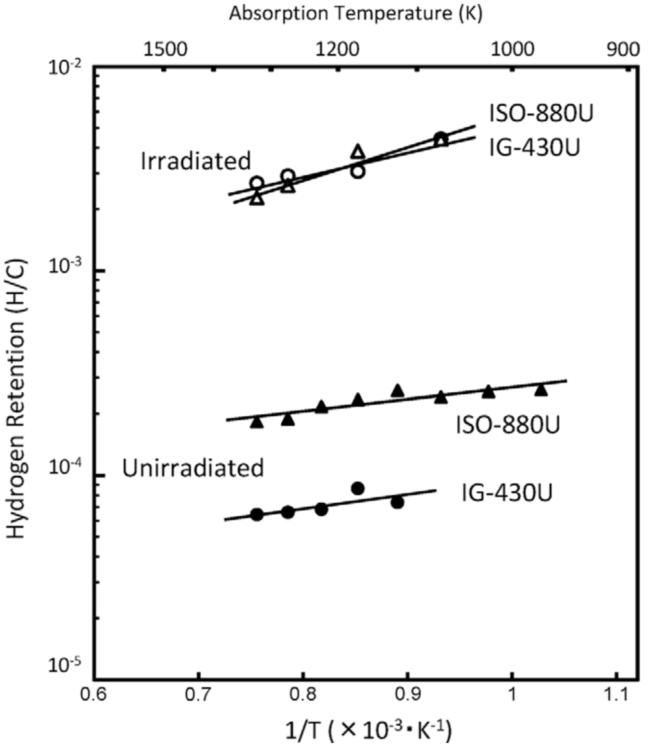

Fig. 2. Temperature dependence of hydrogen retention in graphite before and after neutron irradiation (irradiation fluence: 3.9×10^{23} n/m^2 (0.047 dpa), absorption temperature: 1273 K, equilibrium pressure: ∼10 kPa).

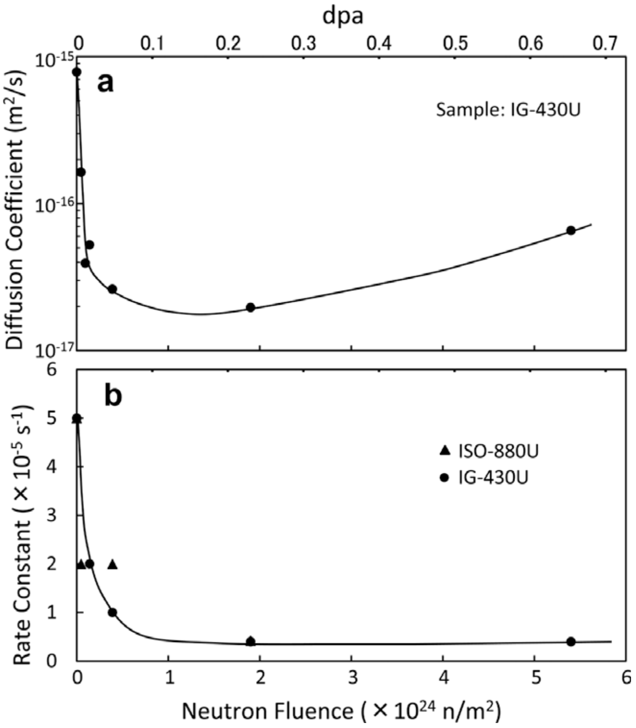

Fig. 3. Change of absorption kinetics of hydrogen into graphite irradiated with neutrons at various fluences (sample: IG-430U and ISO-880U, absorption temperature: 1273 K). (a) Diffusion coefficients of hydrogen into graphite (b) Absorption rate constants for penetration into graphite intercalations.

Fig. 3(b) shows the hydrogen absorption rate constants for penetration into graphite intercalations derived from the second stage of hydrogen pressure decrease. It corresponds to the absorption rate into trap 1 sites. The values of rate constants tend to decrease with increasing neutron fluences up to 0.1 dpa, namely, indicating that the penetration into graphite intercalations is suppressed in neutron-irradiated graphite. Since the reaction of penetration process is basically a first-order reaction, the rate constants should reflect the trap binding energy rather than the concentration of trapping sites. Hence, the reduction of rate constants may be attributed to the appearance of high energy sites (trap 1), around the surface region of a crystallite, and it will prevent the inward penetration of hydrogen. This hypothesis is consistent with the result of nearly unchanged rate constants at high fluences, although increasing rate constants would be anticipated due to the widening of the space of graphite intercalations with increasing neutron fluences. The change of rate constants supports the assessment, in which the hydrogen absorption of the second stage (penetration into trap 1 sites) is controlled by a first-order reaction and not by a diffusion process.

3.3. Pre-annealing effects

Hydrogen absorption measurements were performed in order to investigate the nature of trapping sites, such as thermal stability and annealing effects on the neutron-irradiated samples. Heat treatment, or pre-annealing, was performed at 1273–1873 K for two hours in vacuum prior to hydrogen gas exposure. Typical pressure decrease for ISO-880U irradiated at 0.047 dpa and annealed at various temperatures is shown in Fig. 4. One can recognize that the equilibrium pressures become higher for higher annealing temperatures, and this indicates that the total hydrogen retention decreases with increasing of annealing temperatures. A decrease of the first stage hydrogen absorption can be seen in the figure similarly as parabolic curves, while the second stage absorption, or absorption into trap 1, becomes more significant for the samples

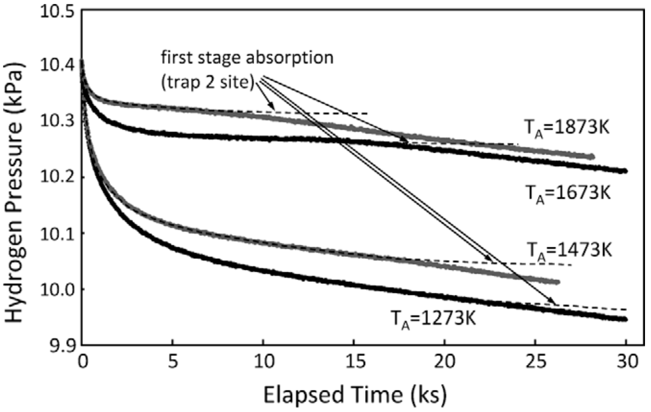

Fig. 4. Pressure change in hydrogen absorption measurements into neutron-irradiated graphite, which were annealed in vacuum at various temperatures, T_A, prior to hydrogen gas exposure (sample: ISO-880U, irradiation fluence: 3.9×10^{23} n/m^2 (0.047 dpa), absorption temperature: 1273 K, equilibrium pressure: ~10 kPa).

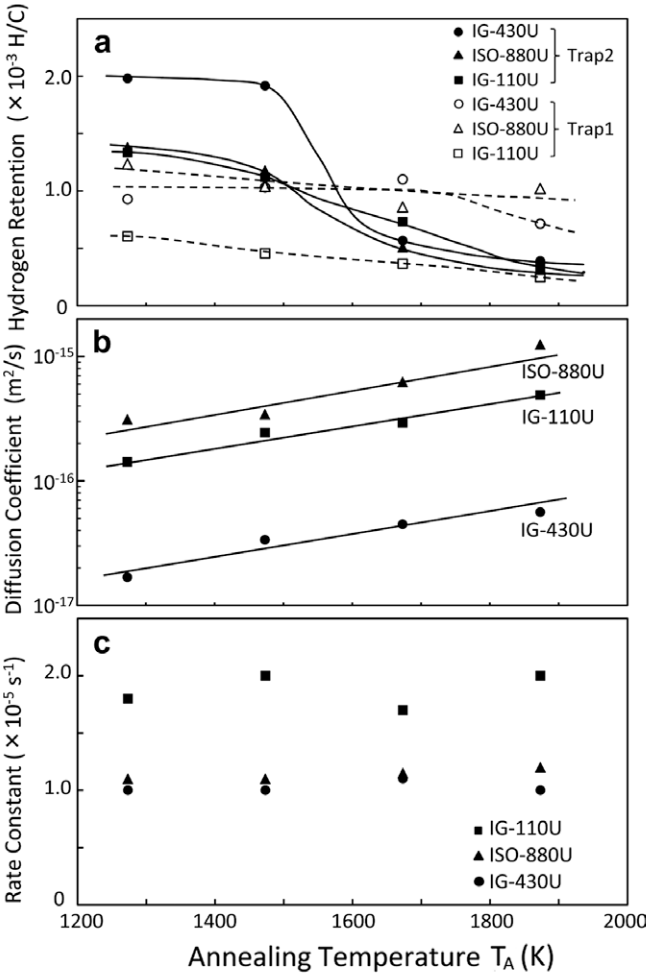

Fig. 5. Change of hydrogen retention and absorption kinetics of hydrogen into neutron-irradiated graphite, which were annealed at various temperatures (irradiation fluence: 3.9×10^{23} n/m^2 (0.047 dpa), absorption temperature: 1273 K, equilibrium pressure: ~10 kPa). (a) Hydrogen retention in neutron-irradiated graphite shown for each trapping site. (b) Diffusion coefficients of hydrogen into graphite. (c) Absorption rate constants for penetration into graphite intercalations.

annealed at higher temperatures. Thus, the pre-annealing of irradiated graphite results in the preferential decrease of trap 2 sites rather than trap 1 sites. The estimated results of hydrogen retention for pre-annealed graphite samples irradiated at 0.047 dpa are plotted for each trapping site in Fig. 5(a). The retention corresponding to trap 2 tends to decrease markedly after the heat treatment above 1473 K, and the values finally became approximately one fifth as large as the retention for the samples annealed at 1273 K, while the retention corresponding to trap 1 is not reduced significantly even for the sample heated at 1873 K. One can conclude that the trap 1 site should be thermally more stable than trap 2.

Fig. 5(b) shows the change of diffusion coefficients of hydrogen for pre-annealed samples measured at an absorption temperature of 1273 K. The diffusion process, as mentioned before, is strongly affected by trapping effects of trap 2. Since the concentration of trap 2 decreased with increasing annealing temperature, the 'apparent' diffusion coefficients should be higher for the samples pre-annealed at higher temperatures. The expectation agrees well with the experimental results. Meanwhile, the rate constant for second stage hydrogen absorption was found not to be changed by pre-annealing (Fig. 5(c)). The hypothesis, by which trap 1 is produced near the surface region of a crystallite to suppress the hydrogen permeation, has been advanced to explain the reduction of absorption rate constant due to neutron irradiation (Fig. 3(b)). Keeping the values of rate constants can be well explained with this hypothesis, since the trap 1 sites remain nearly constant even for high heat treatment temperature. Therefore, the hydrogen permeation into graphite intercalations may be adequate to consider a detrapping process from the trapping sites rather than a dissociation process of hydrogen molecules into atoms.

4. Conclusions

Bulk hydrogen retention and the analysis of absorption kinetics have been studied on isotropic graphite samples irradiated with neutrons at various fluences. The results can be summarized as follows:

(1) Total hydrogen retention in graphite is increased with neutron irradiation fluence, and it reaches the maximum retention at the highest fluence, which are 140 times larger than for unirradiated samples. Neutron irradiation preferably creates trap 2 sites (crystallite edge), at lower fluences. Production of trap 1 site (interstitial cluster loop) appears above 0.017 dpa, and the retention is enhanced above 0.2 dpa.

(2) The enthalpies of hydrogen dissolution into neutron-irradiated graphite increase by a factor of roughly 2–3 compared to those for unirradiated samples. This may be caused by the increase of trap 1 with a high binding energy.

(3) The fist stage of hydrogen absorption, which is assigned to a diffusion process within a graphite filler grain, was strongly affected by the increase of trap 2; consequently, the apparent diffusion coefficient decreased by one fortieth at a damaged level of 0.1 dpa. Further irradiation leads to a higher diffusion coefficient due to the saturation of the concentration of trap 2 and the decrease of the size of diffusion medium, such as reduction of crystallite size and short circuit production.

(4) The second stage of hydrogen absorption, or penetration into graphite intercalations, was suppressed by neutron irradiation. This is ascribed to the appearance of high energy sites (trap1) around the surface region of a crystallite rather than to the increase of concentration of trap 2.

(5) Trap 1 site is thermally stable even after the heat treatment at 1873 K. On the other hand, trap 2 tends to be annealed out above 1473 K.

(6) The apparent diffusion coefficients of hydrogen are increased for pre-annealed samples with increasing annealing temperature. It could be attributed to the decrease of trap 2 by annealing.

(7) The rate constant of hydrogen penetration into graphite intercalations is not changed by pre-annealing. The rate determining step of the hydrogen permeation should be attributed to a detrapping process from the trapping sites (both traps 1 and 2) located around the edge surface of a graphite crystallite.

Neutron irradiation under different conditions is in progress for various types of graphite and CFCs.

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