



Hydrogen trapping in neutron-irradiated graphite

H. Atsumi^{a,*}, A. Muhaimin^a, T. Tanabe^b, T. Shikama^c

^a Department of Electric and Electronic Engineering, Faculty of Science and Engineering, Kinki University, Kowakae 3-4-1, Higashi-Osaka 577-8502, Japan

^b Interdisciplinary Graduate School of Engineering Science, Kyushu University, Fukuoka 812-8581, Japan

^c Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

ARTICLE INFO

PACS:
52.40.Hf

ABSTRACT

Bulk hydrogen retention and the analysis of absorption kinetics have been studied on three brands of graphite irradiated with neutrons at various fluences. Two kinds of hydrogen trapping sites may exist and be additionally produced during irradiation: interstitial cluster loop edge sites (trap 1) and carbon dangling bonds at edge surfaces of crystallites (trap 2). Neutron irradiation preferably creates trap 2 sites at lower fluences and trap 1 sites at a higher fluence above 0.017 dpa. Trap 2 tends to be annealed out at high temperatures, although trap 1 is hardly decreased even at 1873 K. Diffusion coefficients of hydrogen are reduced for 1–2 orders of magnitude after neutron irradiation at 0.047 dpa, although the activation energy of hydrogen diffusion is kept nearly the same level to unirradiated samples.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Graphite and CFCs are still the principal materials for plasma facing walls in current fusion experimental devices and also for divertor plates in ITER due to high thermal conductivity and thermal shock resistivity [1,2]. However, these materials raise the amount of hydrogen recycling and tritium inventory due to their affinity to hydrogen. Hydrogen recycling and tritium inventory are the critical issues for next step fusion reactors which aim to realize long pulse or steady state operation. Moreover, codeposited layers produced by chemically eroded carbon will be the major source of hydrogen and tritium inventory even in a device mainly lined with beryllium and tungsten [3–5]. Especially, carbon and graphite with damaged structure, such as ion or neutron-irradiated samples and carbon dust, retain significantly high amounts of hydrogen [3,6,7]. From the viewpoint of plasma density control and reducing the tritium inventory, it is important to understand the hydrogen behavior in such materials.

Previous studies by the authors of bulk hydrogen retention in neutron-irradiated graphite [6,8] showed that the amount of retained hydrogen increased by 20–50 times and the absorption rate decreased to one seventieth compared to unirradiated samples. After several years, it was ascertained that there should be at least two kinds of trapping sites for hydrogen in unirradiated graphite samples [9–12]. In the most recent work, hydrogen absorption process into neutron-irradiated graphite (ISO-880U) has been investi-

gated focusing on the trapping site identification, pre-annealing the samples, and absorption temperature [13]. In the present study, these behaviors have been estimated on three brands of graphite samples irradiated at higher fluences up to 0.65 dpa.

2. Experimental

The specimens used in this study were three brands of isotropic graphite with different physical properties: IG-110U, IG-430U and ISO-880U (Toyo Tanso Co. Ltd.). They were irradiated in the Japan Materials Testing Reactor (JMTR) at fluences up to 5.4×10^{24} n/m² (>1 MeV) below 473 K. After neutron irradiation, hydrogen absorption into the sample 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 were determined from the pressure decrease in the chamber. The absorption rate constants (D/r^2), which can be regarded as apparent diffusion coefficients, were derived by fitting the pressure curve to a theoretically calculated curve [6].

3. Results and discussion

3.1. Hydrogen retention and trapping site

As above-mentioned, there should be at least two kinds of trapping sites for hydrogen in graphite [9–12]. One is an interstitial cluster loop edge or a solitary carbon dangling bond located in a crystallite with the energy of 4.4 eV (trap 1), and the other is a carbon dangling bond located at the edge surface of a crystallite with

* Corresponding author. Address: Department of Electric and Electronic Engineering, Faculty of Science and Engineering, Kinki University, Kowakae 3-4-1, Higashi-Osaka 577-8502, Japan. Tel.: +81 6 6721 2332x4367; fax: +81 6 6723 2721.
E-mail address: atsumi@le.kindai.ac.jp (H. Atsumi).

the absorption enthalpy of 2.6 eV (trap 2) [10,12]. Hydrogen absorption into graphite appeared to take place in two stages. The first stage is the pressure decrease caused by absorption to trap 2, where the curve can be fitted well with the theoretical curve assuming a diffusion-controlled process which approximately obeys a parabolic function at the initial stage and an exponential function at the latter stage [6]. The second stage of absorption starts near the termination of the first stage, and the net pressure decrease during this stage simply followed an exponential function, since the rate of hydrogen penetration into a small crystallite was controlled by first-ordered chemical reaction, which caused by dissociation at a surface or detrapping from trap 2 [10].

A typical absorption curve obtained in the present work is shown in Fig. 1(b) with the data for an unirradiated sample shown for comparison in Fig. 1(a). In the present results measured for the irradiated samples at hydrogen pressure above 10 kPa, the theoretical curve could represent only the initial stage of absorption, while the curves fitted well with theoretical curves in the case around 1 kPa in previous works determined for unirradiated samples [10,12]. As shown in Fig. 1, the final pressure decrease of the first stage to the equilibrium state corresponds to the amount of hydrogen retained in trap 2, and the discrepancy between the experimental and theoretical curves corresponds to hydrogen trapped in trap 1. The absolute pressure decrease corresponding to trap 1 for the irradiated sample (0.1 kPa, Fig. 1(b)) appears to be 1.5 times that for the unirradiated sample (0.15 kPa, Fig. 1(a)). However, since the mass of the unirradiated sample is 20 times larger than that of the irradiated one, the hydrogen retention per unit mass in the irradiated sample is in fact approximately thirty times larger as shown in Fig. 2(a). It is also evident from Fig. 1 that the abundance ratio of trap 1 is about 5 times higher for the irradiated sample. Also from the theoretical curve in Fig. 1, the derived absorption

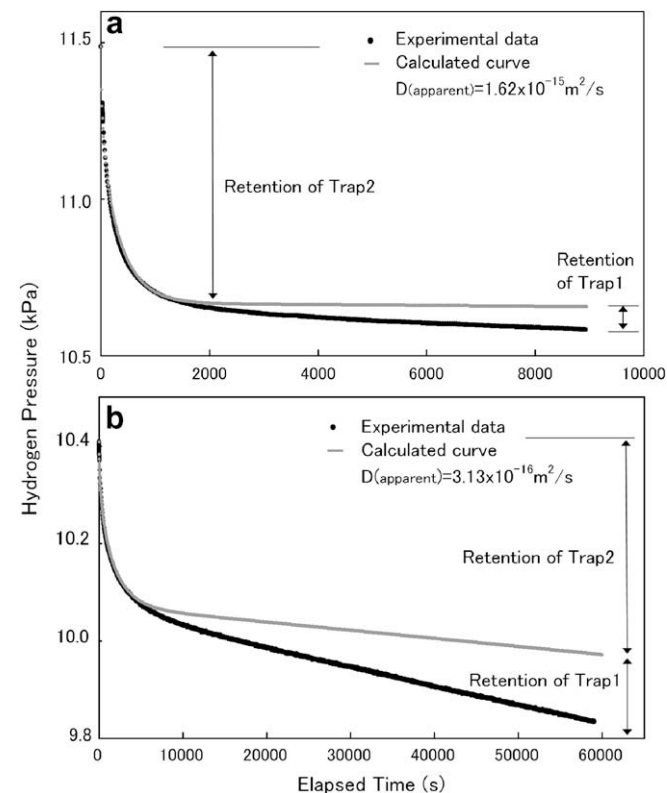


Fig. 1. Typical pressure change in hydrogen absorption measurements into graphite and the derivation of site occupancy (ISO-880U, absorption temperature: 1273 K). (a) unirradiated, (b) irradiated at 3.9×10^{23} n/m² (~450 K).

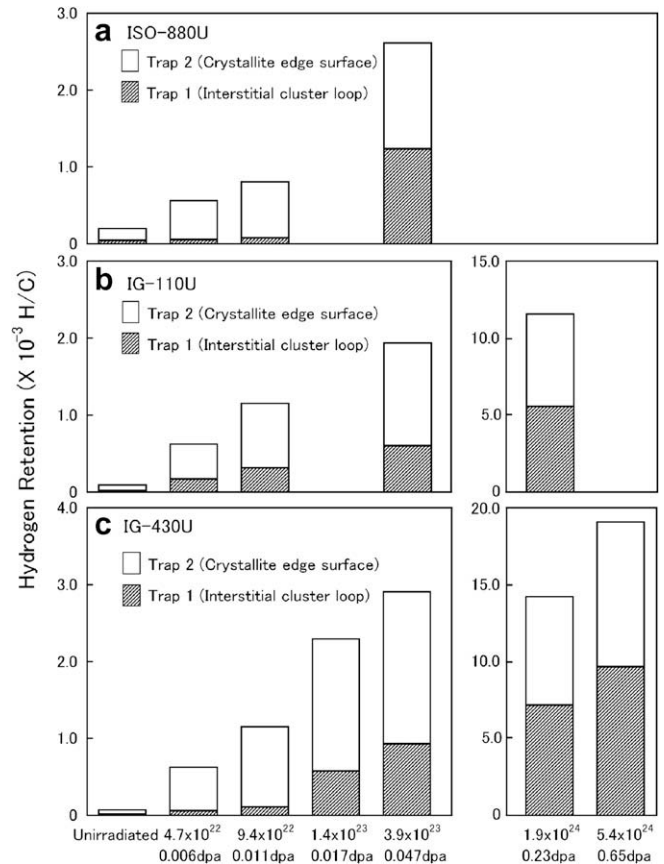


Fig. 2. Hydrogen retention in neutron-irradiated graphite shown for each trapping site (absorption temperature: 1273 K, Equilibrium pressure: ~10 kPa). (a) ISO-880U, (b) IG-110U, (c) IG-430U.

rate, or diffusion coefficient, is about 5 times smaller for the irradiated sample.

Hydrogen retention in neutron-irradiated graphite determined for each trapping site is shown for different neutron fluences in Fig. 2. The total retention increases with the irradiation fluence. At lower neutron fluences below 0.011 dpa, the increase is mainly due to the increase of trapping in trap 2, while at higher fluences above 0.23 dpa, retention consists of nearly the same quantity of trap 1 and trap 2 retentions. The observed increase of trap 2 retention with increasing neutron fluence is consistent with the previously observed decrease in crystallite size with increasing fluence [8]. The decrease in crystallite size is, however, not monotonic with neutron fluence. The crystallite size decreases rapidly up to a fluence of 0.017 dpa. For further increasing fluence it decreases only very slowly. On the other hand, since the defects of trap 1, or interstitial cluster loops, are necessary to accumulate point defects [14], the retention in trap 1 will increase abruptly above a critical fluence. It may appear at 0.017 dpa for IG-430U (Fig. 2(c)).

3.2. 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 2 h in vacuum prior to hydrogen gas exposure. Typical pressure decrease was shown in Fig. 3. It can be seen that the retention corresponding to trap 2, or the initial stage of pressure decrease, was reduced and the trap 1 retention, or the latter stage, became more

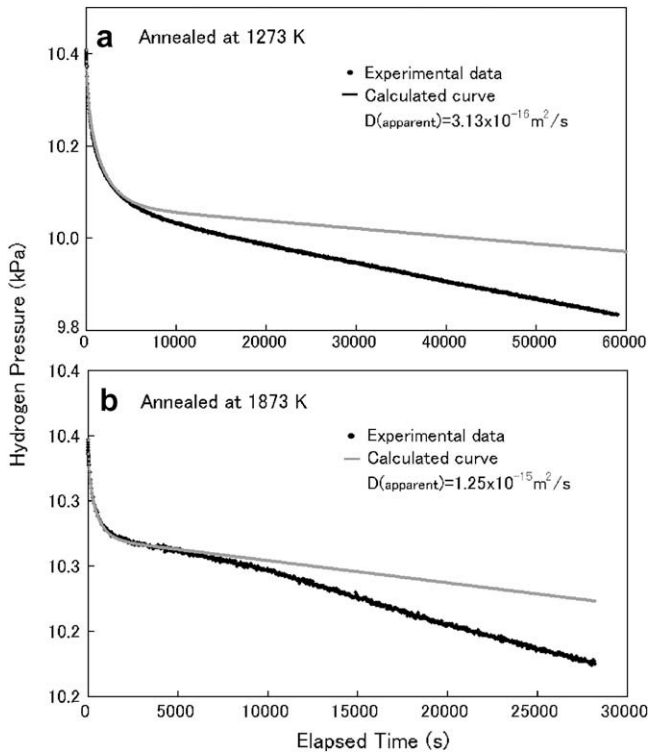


Fig. 3. Pressure change in hydrogen absorption measurements into graphite pre-annealed at different temperatures (ISO-880U, absorption temperature: 1273 K). (a) pre-annealed at 1273 K for 2 h, (b) pre-annealed at 1873 K for 2 h.

prominent (Fig. 3(b)). The process of absorbing hydrogen into trap 2 is controlled by crystallite boundary diffusion with a sequence of trapping and detrapping [9,10,12]. Since the process is not 'true' hydrogen diffusion, the authors have named this behavior as 'apparent' diffusion [10,12]. If the number of trap 2 decreases by pre-annealing, the apparent diffusion coefficient will increase due to the reduction of trapping frequency. In fact, the value increased four times of magnitude by pre-annealing, and this hypothesis should be consistent (Fig. 3(a) and (b)). On the other hand, the activation energy of diffusion may not be influenced, unless the nature of trapping sites changes by progression of irradiation or pre-annealing treatments. As for trap 1, it is highly suggestive that the triggered time shows around 5000 s and the amount does not changed much even for pre-annealing at high temperature.

The retention obtained for pre-annealed samples is shown in Fig. 4. For all the samples, the retention which corresponds to trap 2 tends to decrease with the increase of pre-annealing temperature. This indicates that most of the trap 2 sites induced by neutron irradiation will be annealed out at high temperatures. However, the trap 2 sites may not be completely annealed out, since the retention was still twice as high as the amount obtained for the unirradiated sample, which was also pre-annealed at 1873 K (Fig. 2). On the other hand, retention in trap 1 tends to remain relatively high even after the heat treatment at 1873 K except for IG-110U (Fig. 4(b)). One can conclude the trap 1 sites should be thermally more stable rather than trap 2, although the trap 1 for IG-110U might have different stability from other two samples, since the number of trap 1 started to increase at a lower damage than those for IG-430U and ISO-880U (Fig. 2(b)). Since the retention for trap 1 sites hardly decreased, it is anticipated that highly damaged graphite or carbon leads to high hydrogen retention even at a very high temperature.

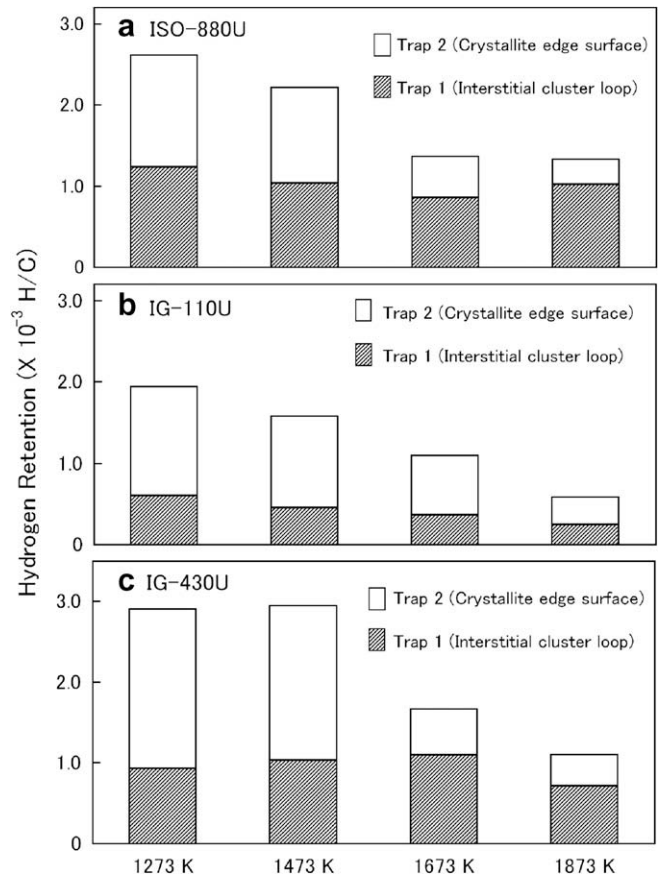


Fig. 4. Comparison of hydrogen retention for neutron-irradiated graphite pre-annealed at various temperatures (absorption temperature: 1273 K, equilibrium pressure: ~10 kPa). Pre-annealing was performed at 1273–1873 K in vacuum for 2 h prior to hydrogen exposure. (a) ISO-880U, (b) IG-110U, (c) IG-430U.

3.3. Diffusion coefficients

Diffusion coefficients mentioned in this work will be considered only as 'apparent' values – not true diffusion coefficients, where trapping and detrapping phenomena are strongly affected. In fact, the pressure decrease in the present experiments can be explained well with a diffusion-controlled process; however, the diffusion coefficients of hydrogen in a neutron-irradiated sample were drastically reduced [6]. The apparent diffusion coefficients

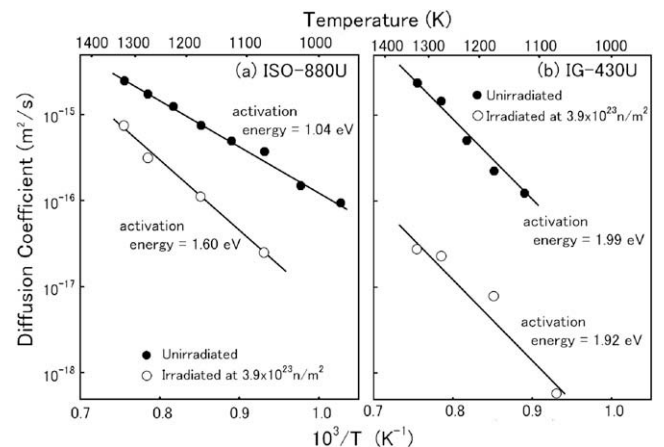


Fig. 5. Arrhenius plot of apparent diffusion coefficients of hydrogen in graphite (equilibrium pressure: ~10 kPa). (a) ISO-880U, (b) IG-430U.

obtained in the present study are plotted in Fig. 5. Although the reduction of diffusion coefficients can be recognized for both samples, the activation energies, or slopes, show a different manner. The activation energy of diffusion for ISO-880U shows a higher value (1.60 eV), and that for IG-430U shows a similar value (1.92 eV) compared to each unirradiated sample. The result obtained for ISO-880U does not support the above-mentioned hypothesis of fixed activation energy for the same nature of trapping sites, although the activation energy of 1.60 eV is still smaller than that for IG-430U. We can assume the following two reasons for the change of activation energy of hydrogen diffusion in ISO-880U samples:

- (1) The trap 2 additionally produced by neutron irradiation has a higher activation energy than that for original trap 2 existed in an unirradiated sample.
- (2) The diffusion coefficients at 1273 K and 1323 K are increased due to the partial annealing out of trap 2 during absorption measurements.

The latter seems to be probable, since the diffusion coefficients were increased with the reduction of trapping sites, although the annealing temperature is much higher than the absorption temperature (Fig. 3). Further experiments are needed to ascertain the appreciation of these candidates.

4. Conclusions

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

- (1) Neutron irradiation preferably created trap 2 sites (crystal-lite edge), at lower fluences up to 0.011 dpa, and the production of trap 1 site (interstitial cluster loop) was enhanced above 0.017 dpa.
- (2) Hydrogen retention for trap 2 was decreased by pre-annealing treatment before hydrogen gas charge, while trap 1 hardly decreased even at 1873 K. It is anticipated that highly damaged graphite or carbon may keep high hydrogen retention even at a very high temperature.
- (3) The ‘apparent’ diffusion coefficients were reduced by neutron irradiation. On the other hand, the activation energy of hydrogen diffusion was kept nearly the same level to unirradiated samples.

References

- [1] R. Aymar et al., *J. Nucl. Mater.* 258–263 (1998) 56.
- [2] G. Kalinin et al., *Fusion Eng. Des.* 55 (2001) 231.
- [3] R.A. Causey, *J. Nucl. Mater.* 300 (2002) 91.
- [4] C. Stan-Sion et al., *J. Nucl. Mater.* 290–293 (2001) 491.
- [5] G. Federici et al., *J. Nucl. Mater.* 313–316 (2003) 11.
- [6] H. Atsumi, M. Iseki, T. Shikama, *J. Nucl. Mater.* 191–194 (1992) 368.
- [7] H. Yoshida et al., *Fusion Eng. Des.* 70 (2004) 201.
- [8] H. Atsumi, M. Iseki, T. Shikama, *J. Nucl. Mater.* 233–237 (1996) 1128.
- [9] H. Atsumi, *J. Nucl. Mater.* 307–311 (2002) 1466.
- [10] H. Atsumi, *J. Nucl. Mater.* 313–316 (2003) 543.
- [11] H. Atsumi, *Phys. Scr.* T103 (2003) 77.
- [12] H. Atsumi, K. Tauchi, *J. Alloys Compd.* 356–357 (2003) 705.
- [13] H. Atsumi, N. Shibata, T. Tanabe, T. Shikama, *Phys. Scr.* T128 (2007) 72.
- [14] K. Niwase, M. Sugimoto, T. Tanabe, F.E. Fujita, *J. Nucl. Mater.* 155–157 (1988) 303.