ELSEVIER

Journal of Nuclear Materials 307–311 (2002) 1466–1470

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Hydrogen bulk retention in graphite and kinetics of diffusion

H. Atsumi *

Department of Nuclear Engineering, Faculty of Science and Engineering, Kinki University, Kowakae 3-4-1, Higashi-Osaka, Osaka 577-8502, Japan

---

Abstract

Molecular hydrogen absorption into graphite has been studied in order to obtain information on the 'true' hydrogen diffusion coefficient in graphite, oxygen effect and the mechanism of hydrogen trapping, which should be important issues on estimating hydrogen retention and recycling in plasma facing graphite and CFC. Hydrogen may permeate into a filler grain in the form of hydrogen molecules, diffuse through crystallite boundaries, and may finally be trapped as hydrogen atoms at the edge surface of a crystallite. The diffusion coefficient can be given as $D\ (\mathrm{m^2/s}) = 3.3 \times 10^{-10}(-1.3\ \mathrm{eV}/kT)$, when the trapping effect does not exist. The simulation with mass balance equations can reproduce change of apparent diffusion coefficients.

---

1. Introduction

Graphite and carbon-based materials are attractive candidates for the plasma facing components in current and the next fusion experimental devices such as ITER [1,2]. As well known, these materials cause high hydrogen recycling and high tritium inventory. Hydrogen recycling is one of the critical issues for the next experimental reactors which will realize long pulse or steady state operation. Bulk hydrogen retention seems to dominate the hydrogen retention in graphite and carbon-based materials at temperatures above 1000 K [3–5], instead of hydrogen implanted in the subsurface region which would be released below the temperature.

From this point of view, numerous studies have been performed concerning the hydrogen retention in the bulk of graphite exposed to hydrogen gas and the hydrogen diffusion [6–18]. However, in these results, the amount of the retained hydrogen are significantly dependent on the brands of graphite [11–13], and the pressure dependences are also quite different in each study (observed: [7,12,17], not observed: [6]). Moreover, hydrogen diffusion coefficients in graphite show a discrepancy of five orders of magnitude (to be mentioned in discussion). Attempts to interpret the complicated phenomena of hydrogen behavior in graphite have been recently made [18,19], and the nature of hydrogen trapping is going to be identified.

In the present study, following key issues to estimate hydrogen bulk retention and hydrogen recycling have been investigated, which are (1) true diffusion coefficient of hydrogen in graphite, (2) oxygen effect on hydrogen retention and diffusion, (3) the mechanism of hydrogen trapping and detrapping in graphite and (4) modeling of hydrogen absorption, transport and desorption.

2. Experimental

The specimens used in this study were several brands of isotropic graphite such as IG-110U, IG-430U, ISO-880U (Toyo Tanso Co. Ltd.) and ATJ (Union Carbide Corp.). The specimens used in each measurement were ≈6 g consisting of several pieces of $5 \times 33 \times 1\ \mathrm{mm}^3$ sheets, although the dimensions of the specimen influenced neither hydrogen retention nor the absorption rate. Prior to hydrogen gas exposure, these specimens were annealed at a given temperature of 1373–1823 K for 1 h in vacuum to desorb the occluding gas. After the

---

* Tel.: +81-6 6721 2332x4367; fax: +81-6 6723 2721.

E-mail address: atsumi@ned.kindai.ac.jp (H. Atsumi).

0022-3115/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(02)01069-3

estimation of the annealing effect, the outgassing temperature was fixed to be 1823 K. Hydrogen retention and absorption rates were evaluated by the 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 pressure range of the experiments was 0.02–40 kPa. Hydrogen transport in a graphite grain was simulated by numerical calculation.

3. Results and discussion

3.1. The nature of hydrogen trapping (oxygen effect)

In order to estimate the nature of hydrogen trapping, hydrogen absorption was examined for graphite samples having been for long period (nine years) in the air. The amounts of absorbed hydrogen (hydrogen bulk retention) were evaluated after 1 h degassing (Fig. 1(a)), and the apparent diffusion coefficients proportional to absorption rate constants, D/r^2, are shown in Fig. 1(b). Since the process of hydrogen absorption appears to be controlled by diffusion process [11,17], absorption rate constants were defined as the quotient of apparent diffusion coefficient with the square of the size of diffusing medium (radius of filler grain). After the outgassing below 1573 K, no hydrogen absorption took place. The hydrogen absorption started from the outgassing temperature of 1573 K, and the value of the bulk retention became similar to that of the fresh specimen (produced and measured in the same year, 1992) after the outgassing at 1823 K. Hydrogen absorption was very rapid for the sample outgassed at 1573 K. The absorption rate decreased with increasing of outgassing temperature and eventually absorption rate became almost equal to the corresponding value at 1823 K for the fresh sample studied in 1992. Edge surface of graphite lattice is chemically active to adsorb various molecules, such as hydrogen, oxygen, water and organic compounds. Organic compounds would be desorbed out at relatively low temperatures, and most of hydrogen released out at around 1400 K [7,14]. Hence, chemical species desorbed at higher temperature are generally CO and CO_2 [20] (O_2 cannot be released from chemically bonded sites, since the binding energy of C–O is larger than that of C–C), and trapping sites will bind oxygen atoms. Therefore, if oxygen atoms forestall to occupy trapping sites, the sites will not show affinity for hydrogen atoms. Consequently, it will increase diffusion coefficient due to lack of trapping effects. As described here, trapping sites for hydrogen atoms should be also for oxygen atoms.

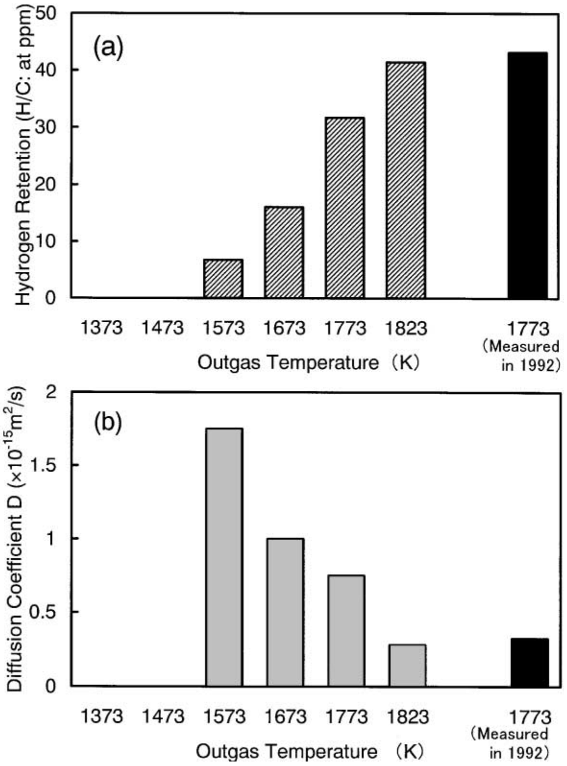

Fig. 1. Hydrogen bulk retention and apparent diffusion coefficients in graphite having been in the air for a long period (sample: ATJ, exposure temperature: 1273 K, hydrogen pressure: 14 kPa, outgassed time: 1 h): (a) hydrogen retention and (b) diffusion coefficients.

Kanashenko et al. [18] and Chernikov et al. [19] have suggested that two kinds of trapping sites exist in graphite, a low-energy site (2.3 eV) and a high-energy site (4.4 eV). According to their studies, the low-energy sites correspond to 'usual C atoms at the edge of crystallite' due to their energy [21], and the high-energy sites correspond to 'submicroscopic interstitial clusters'. It seems that the former has pressure dependency and the latter does not have, since the low-energy trapping will make equilibrium state of trapping and detrapping according to the ambient pressure, on the other hand, the high-energy sites will trap all of the hydrogen atoms until the sites become fully occupied. The concentration of the low-energy trapping sites should be much higher in graphite, on the other hand, the number of high-energy trapping sites will increase in graphite samples irradiated with neutrons or energetic ions. Since the data were obtained from un-irradiated one and measured at relatively high pressures in present work, the low-energy traps must be highly predominant in hydrogen bulk retention. Although, the author have insisted that the hydrogen retention correlated with the degree of graphitization, after the paper [15] was published in 1996, he has suggested that hydrogen atoms were trapped at the edge surface of crystallite due to the better correlation between hydrogen retention and the surface area of prism (edge) plane. It is consistent with the hypothesis proposed by Chernikov et al. [19]. It should be difficult for an oxygen atom to reach interstitial clusters from ambience at a low temperature due to its atomic or molecular size. In conclusion, trapping sites for hydrogen and oxygen should be edge surface of crystallite.

3.2. Pressure dependence of hydrogen absorption

The author showed that hydrogen absorption rate had strong dependence on hydrogen exposure pressure [17]. The hydrogen absorption rates are small at low hydrogen pressures, and large at high hydrogen pressures. In order to ascertain whether the activation energies are different at various hydrogen pressures or not, temperature dependence of absorption rates have been examined at the lowest and the highest pressures in this experimental range (Fig. 2). Although the absorption rates for these two pressures deviate roughly 15 times, the slopes, i.e. activation energies, are similar value (roughly 1.3 eV) in the three samples. This indicates the diffusion process, which controls hydrogen absorption, does not change between low and high pressures (i.e. low and high concentration of hydrogen). Since the trapping is rather deep (i.e. having high activation energy), the migration of hydrogen appears to be suppressed especially at low concentration (at low concentration, traps with binding energy of 2.3–2.9 eV will be effective, but at extremely low concentration, traps with higher binding energy of 4.4 eV may affect diffusion).

3.3. Diffusion mechanism

Based on the results obtained from this work, a hydrogen transport model in graphite under a relatively high hydrogen pressure such as >20 Pa has been developed. Fig. 3 shows a schematic illustration of this model. In the experiments, hydrogen gas can reach the surface of each filler grain through open pores keeping the ambience due to its porous structure. Subsequently, it will penetrate into filler grain by the mechanism of diffusion. In the diffusion process, the medium will be each filler grain. Since the heat of solution of hydrogen in graphite is 1.13 eV [22], energy difference between those for ambient hydrogen molecules and trapped hydrogen atoms will be this value. The activation energy of apparent diffusion of hydrogen derived from hydrogen absorption experiments is 1.3 eV as mentioned in the previous section. On the other hand, the activation energy of apparent diffusion derived from hydrogen desorption experiments is 2.6 eV (Atsumi et al. [7]) or 2.9 eV (Causey et al. [3]). Considering these energies, any energy barrier cannot be realized at grain surface, while an energy barrier can be found at trapping sites. It suggests that hydrogen can diffuse to trapping sites with the form of molecule without dissociation at the grain surface, and then, it is dissociated and bound at trapping sites.

These phenomena are numerically simulated with the following mass balance equations referred to the works by Morita and Tsuchiya [23,24].

$$\frac{\mathrm{d}N(r,t)}{\mathrm{d}t} = D\nabla^2 N(r,t) + \Sigma_\mathrm{d} N_\mathrm{t}(r,t) - \Sigma_\mathrm{t} N(r,t) C(r,t), \tag{1}$$

$$\frac{\mathrm{d}N_\mathrm{t}(r,t)}{\mathrm{d}t} = -\Sigma_\mathrm{d} N_\mathrm{t}(r,t) + \Sigma_\mathrm{t} N(r,t) C(r,t), \tag{2}$$

$$\frac{\mathrm{d}C(r,t)}{\mathrm{d}t} = \Sigma_\mathrm{d} N_\mathrm{t}(r,t) - \Sigma_\mathrm{t} N(r,t) C(r,t), \tag{3}$$

where $N(r,t)$ is the local concentration of free hydrogen atom, $N_\mathrm{t}(r,t)$ is that of trapped hydrogen atom, $C(r,t)$ is

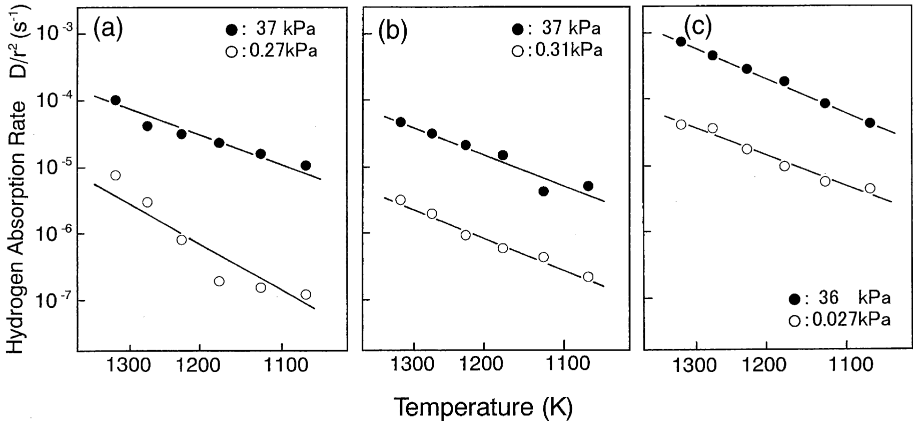

Fig. 2. Temperature dependence of hydrogen absorption rates into graphite exposed at different hydrogen pressures: (a) IG-110U, (b) IG-430U and (c) ISO-880U.

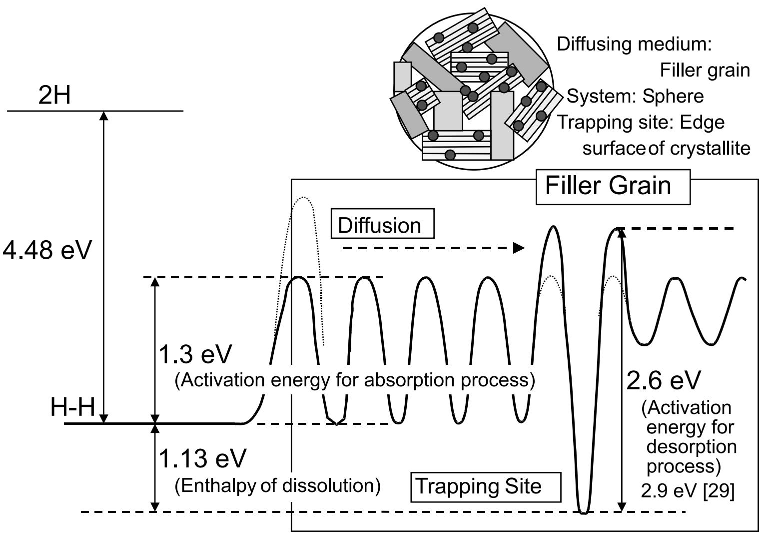

Fig. 3. Schematic illustration of the proposed model on hydrogen diffusion in graphite.

the concentration of vacant trap, D is the true diffusion coefficient of free hydrogen, Σ_d is the thermal detrapping rate constant for trapped hydrogen and Σ_t is the trapping rate constant for free hydrogen. The simulation was performed numerically with 100 divided regions under an assumption of spherical system (presumed by the shape of filler grains), while Morita et al. have solved analytically. If hydrogen diffuses with the form of a molecule, the surface concentration of free hydrogen, $N(R_0, t)$, will be proportional to the hydrogen gas pressure. Assuming the detrapping to be negligibly small, the apparent diffusion coefficients could be derived from the change of the total amount of the trapped hydrogen. The results are shown in Fig. 4 as a function of the hydrogen pressure. The experimental data were obtained

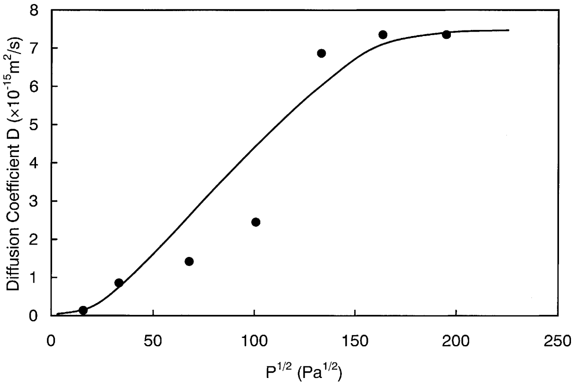

Fig. 4. Apparent diffusion coefficients versus hydrogen pressure and their numerical simulation (sample: IG-110U, temperature: 1273 K, closed circle: experimental value, bold curve: numerical simulation).

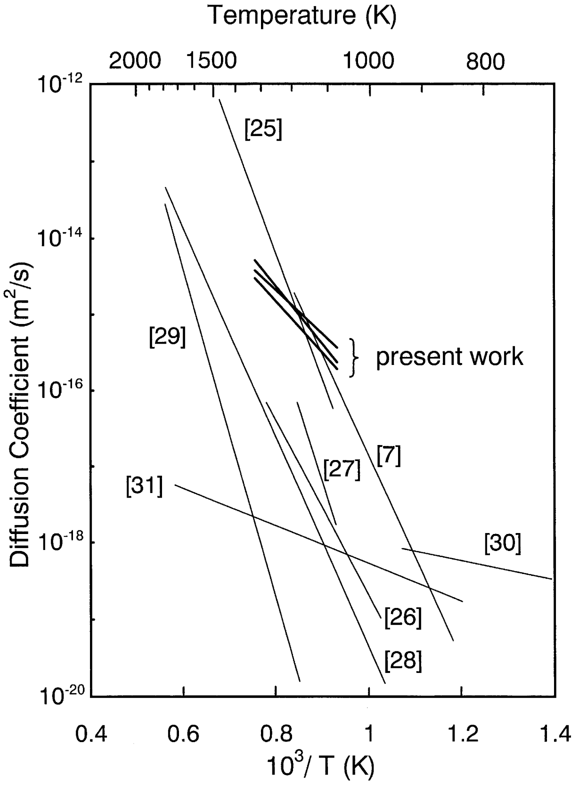

Fig. 5. True hydrogen diffusion coefficients obtained in the present study and comparison of values reported in Refs. [7,25–31].

from IG-110U (grain radius: 7 μm) at 1273 K [17]. Although there is a discrepancy between the experimental data and the simulated curve, the change of apparent diffusion coefficients with hydrogen pressure could be certainly confirmed. In the case, true hydrogen diffusion, which would correspond to the 'crystallite boundary' diffusion of hydrogen molecules, could be evaluated as 7.5×10^{-15} m^2/s.

True diffusion coefficients of hydrogen for three samples are shown in Fig. 5 applying the same estimation to each measuring temperature (1073, 1123, 1173, 1273 and 1323 K) with a comparison of reported diffusion coefficients. Since the data obtained here correspond to 'crystallite boundary' diffusion of hydrogen molecules within each filler grain, the activation energy is the half of other reported energies and the coefficients themselves are relatively high. The diffusion coefficient, D, can be roughly expressed as follows,

$$D\ (\mathrm{m^2/s}) = 3.3 \times 10^{-10}\left(\frac{-1.3\ \mathrm{eV}}{kT}\right). \tag{4}$$

Other reported values in Fig. 5 show high activation energies (2.3–4.4 eV), which are reflected the trap binding energy, except two data seemed to show atomic diffusion within intercalations of graphite lattice [30,31].

4. Conclusions

The hydrogen bulk retention and absorption rates have been examined for various conditions. And the diffusion behavior was simulated with numerical analysis. The results are summarized as follows:

(1) Hydrogen would be trapped at the edge surface of crystallites existing in a filler grain when graphite samples are exposed to hydrogen gas at relatively high pressure such as >20 Pa.
(2) The trapping site can also be occupied with an oxygen atom. In such the case, the site will not show affinity for a hydrogen atom.
(3) Hydrogen will be able to permeate into a filler grain with keeping the form of hydrogen molecule and diffuse through 'crystallite boundaries', and finally trapped at edge surface after dissociation at the place.
(4) The 'crystallite boundary diffusion' can be expressed as $D\ (\mathrm{m^2/s}) = 3.3 \times 10^{-10}(-1.3\ \mathrm{eV}/kT)$ when the trapping effect can be negligible. The value may change due to the difference of the grain structure, the manufacturing conditions, the raw materials and so on.
(5) The absorption and hydrogen transport in graphite were simulated with mass balance equations. Change of apparent diffusion coefficients with hydrogen pressure could be well reproduced.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research by Japan Society for the Promotion of Science.

References

[1] R. Aymar et al., J. Nucl. Mater. 258–263 (1998) 56.
[2] G. Kalinin et al., Fus. Eng. Des. 55 (2001) 231.
[3] R.A. Causey, J. Nucl. Mater. 162–164 (1989) 151.
[4] A.P. Zakharov et al., J. Nucl. Mater. 241–243 (1997) 52.
[5] R.-D. Penzhorn et al., J. Nucl. Mater. 288 (2001) 170.
[6] R.A. Causey, M.I. Baskes, K.L. Wilson, J. Vac. Sci. Technol. A 4 (1986) 1189.
[7] H. Atsumi, S. Tokura, M. Miyake, J. Nucl. Mater. 155–157 (1988) 241.
[8] W.R. Wampler et al., J. Nucl. Mater. 176&177 (1990) 983.
[9] E. Hoinkis, J. Nucl. Mater. 182 (1991) 93.
[10] E. Hoinkis, J. Nucl. Mater. 183 (1991) 9.
[11] H. Atsumi, M. Iseki, T. Shikama, J. Nucl. Mater. 191–194 (1992) 368.
[12] H. Atsumi, M. Iseki, T. Shikama, J. Nucl. Mater. 212–215 (1994) 1478.
[13] H. Kwast et al., J. Nucl. Mater. 212–215 (1994) 1472.
[14] E. Denisov et al., J. Nucl. Mater. 233–237 (1996) 1218.
[15] H. Atsumi, M. Iseki, T. Shikama, J. Nucl. Mater. 233–237 (1996) 1128.
[16] A.V. Markin, A.E. Gorodetsky, A.P. Zakharov, J. Nucl. Mater. 248 (1997) 34.
[17] H. Atsumi, M. Iseki, J. Nucl. Mater. 283–287 (2000) 1053.
[18] S.L. Kanashenko et al., J. Nucl. Mater. 233–237 (1996) 1207.
[19] V.N. Chernikov et al., J. Nucl. Mater. 264 (1999) 180.
[20] P. Grosse et al., Mater. Sci. Eng. B 61&62 (1999) 58.
[21] J.P. Redmond, P.L. Walker Jr., J. Phys. Chem. 64 (1960) 1093.
[22] T. Tanabe, H. Atsumi, J. Nucl. Mater. 209 (1994) 109.
[23] K. Morita, B. Tsuchiya, J. Nucl. Mater. 248 (1997) 27.
[24] B. Tsuchiya, K. Morita, J. Nucl. Mater. 227 (1996) 195.
[25] T.S. Elleman, unpublished work at General Atomic, San Diego, CA, USA.
[26] M. Saeki, J. Nucl. Mater. 131 (1985) 32.
[27] V. Malka et al., Proceedings of the Tritium Technology in Fusion, Fission and Isotopic Applications, ANS National Topical Meetings, Ohio, 1980, p. 102.
[28] H.D. Röhrig et al., J. Am. Ceram. Soc. 155–157 (1988) 241.
[29] R.A. Causey et al., Carbon 17 (1979) 323.
[30] K. Morita et al., J. Nucl. Mater. 162–164 (1989) 991.
[31] T. Tanabe, Y. Watanabe, J. Nucl. Mater. 179–181 (1991) 231.