Trapping and detrapping of hydrogen in graphite materials exposed to hydrogen gas

Hisao Atsumi[1], Michio Iseki[2] and Tatsuo Shikama[3]

[1] Department of Nuclear Reactor Engineering, Faculty of Science and
Technology, Kinki University, Kowakae 3-4-1, Higashi-Osaka, Osaka 577, Japan

[2] Department of Nuclear Engineering, Faculty of Engineering, Nagoya
University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-01, Japan

[3] The Oarai Branch, Institute for Materials Research, Tohoku University,
Narita-cho, Oarai-machi, Higashiibaraki-gun, Ibaraki 311-13, Japan

Measurements of hydrogen solubility have been performed for several unirradiated and neutron-irradiated graphite (and CFC) samples at temperatures between 973 and 1323K under a ~10 kPa hydrogen atmosphere. The hydrogen dissolution process has been studied and it is discussed here. The values of hydrogen solubility vary substantially among the samples up to about a factor of 16. A strong correlation has been observed between the values of hydrogen solubility and the degrees of graphitization determined by X-ray diffraction technique. The relation can be extended even for the neutron irradiated samples. Hydrogen dissolution into graphite can be explained with the trapping of hydrogen at defect sites (e.g. dangling carbon bonds) considering an equilibrium reaction between hydrogen molecules and the trapping sites. The migration of hydrogen in graphite is speculated to result from a sequence of detrapping and retrapping events with high energy activation processes.

KEYWORDS: graphite, hydrogen retention, reactor irradiation

1. Introduction

Graphites and carbon fiber/carbon composites (CFCs) have been widely applied as plasma facing materials for fusion experimental devices because of their excellent thermal properties. However, they have several disadvantages such as high hydrogen retention and high erosion yields by chemical sputtering and radiation enhanced sublimation. The high hydrogen retention not only makes density control of a plasma become difficult but also is a critical issue for tritium inventory. Hence, it is important to clarify hydrogen behavior in graphite under a fusion reactor operation.

The authors have measured the hydrogen solubility and kinetics of hydrogen absorption for various types of graphite and CFC[1-4]. The solubilities were widely scattered among samples (they differ 16 times at maximum)[3,4], and increased up to 20-50 times due to neutron irradiation[2,4].

In the present study, hydrogen retention and transport in graphite have been discussed based on the data obtained for hydrogen dissolution measurements and hydrogen desorption measurements.

2. Experimental

Samples used in this study were eighteen brands of graphite materials manufactured by eight companies, i.e. : Toyo Tanso (IG-110U, IG-430U, ISO-630U, ISO-880U and CX-2002U), Toyo Carbon (AX-280K, AX-650K and AX-750K), Ibiden (T-4MP, T-6P and ETP-10), Hitachi Chemical (PD-330S and PCC-2S), Ringsdorf Werke (EK-47 and EK-98), POCO Graphite (AXF-5Q1), Union Carbide (ATJ) and Le Carbone Lorraine (CL-5890PT). CX-2002U and PCC-2S are CFC materials, and the others

are isotropic graphites. As a characterization of the samples, lattice constants were determined with an X-ray powder diffraction method detailed elsewhere in the literature[3]. Hydrogen solubility measurements were performed in a temperature range of 973-1323K under a hydrogen atmosphere of ~10 kPa in a constant volume. Some samples (IG-110U, IG-430U, ETP-10 and CX-2002U) were irradiated in the Japan Materials Testing Reactor (JMTR) at fluences up to 6.0×10^{24} n/m^2 (> 1 MeV) at two different temperatures of <473K and 873K. And the effect of neutron irradiation were examined on the hydrogen solubility in graphite.

3. Results and discussion

3.1. Hydrogen solubility in graphites and CFCs

Hydrogen solubilities at 1273K obtained in this study are compared in Fig.1 for all samples. The solubilities differ significantly among the different samples. CFCs
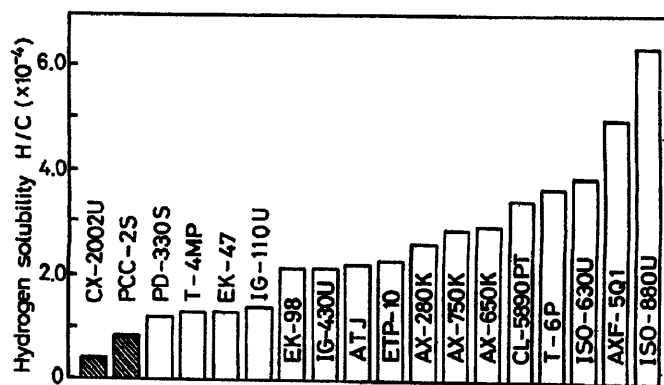

Fig.1. Hydrogen solubilities in graphites and CFCs at 1273K under one atmospheric pressure of hydrogen.

(CX-2002U and PCC-2S) show lower hydrogen solubility when compared to the other materials. On the other hand, isotropic graphites, especially the samples with higher density, finer grains and higher mechanical strength[5] such as ISO-880U (1.90 g/cm³), AXF-5Q1 (1.83 g/cm³) and T-6P (1.91 g/cm³) show higher hydrogen solubilities. The difference of the solubilities between the highest one (ISO-880U) and the lowest one (CX-2002U) amounts approximately to a factor of 16.

3.2. Relation to the crystallographic characteristics of graphites and CFCs

According to Franklin[6], the lattice spacing d002 can be correlated to a degree of graphitization, G, which is

$$G = 1 - 3.41(d_{002} - 3.354)^{1/2} \qquad (1)$$

Fig.2 shows the degrees of graphitization determined from the X-ray powder diffraction technique. The degrees of graphitization are spread in the range of 48-77%. The
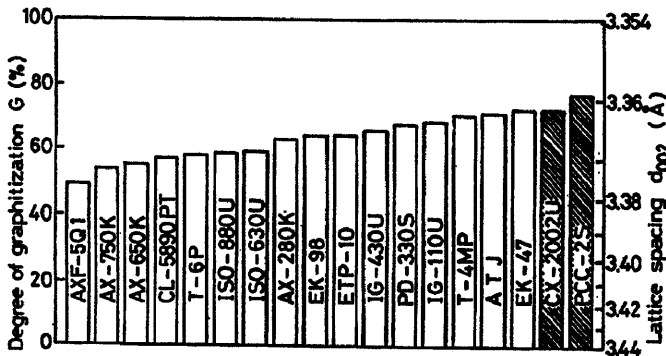

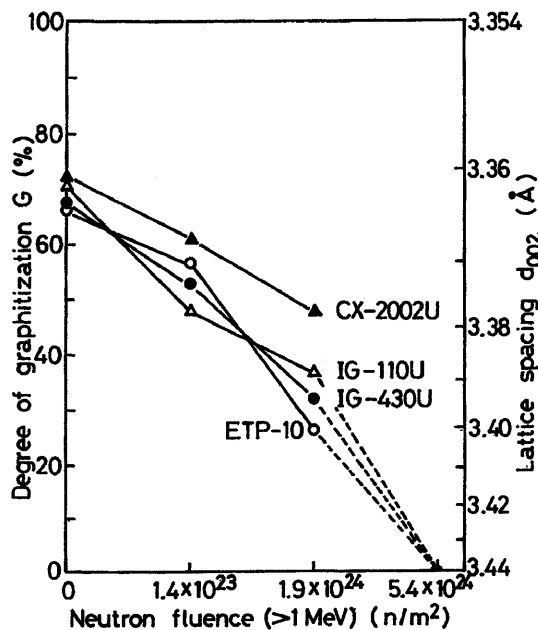Fig.2. Degrees of graphitization measured for graphite and CFC samples.

Fig.3. Changes in the degree of graphitization induced by neutron irradiation.

isotropic graphites, as mentioned before, indicate lower degrees of graphitization, which CFCs show higher values.

It is well-known that the lattice spacing of graphite along c-axis expands by neutron irradiation due to an accumulation of interstitial atoms between the basal planes. Fig.3 gives the lattice spacings and the corresponding degrees of graphitization for neutron-irradiated samples after hydrogen solubility measurements. The lattice spacings of the samples irradiated at 5.4x10²⁴ n/m² actually exceeded 3.44A which was the anticipated value for the distance of carbon atoms in random orientation. Those values of graphitization were regarded as zero degree as a matter of convenience. One can clearly recognize that the degree of graphitization is reduced by neutron irradiation. However the decrease for CX-2002U is less pronounced. The reason could be attributed that the CFC material with highly graphitized components changed smaller in structure as compared with other types of graphite after neutron irradiation.

It can be easily supposed that there are some kinds of correlation between the value of hydrogen solubility in graphites (and CFCs) and the degree of graphitization, since the degree of graphitization was decreased due to neutron irradiation, and, on the other hand, the hydrogen solubility increased considerably[2]. To support this
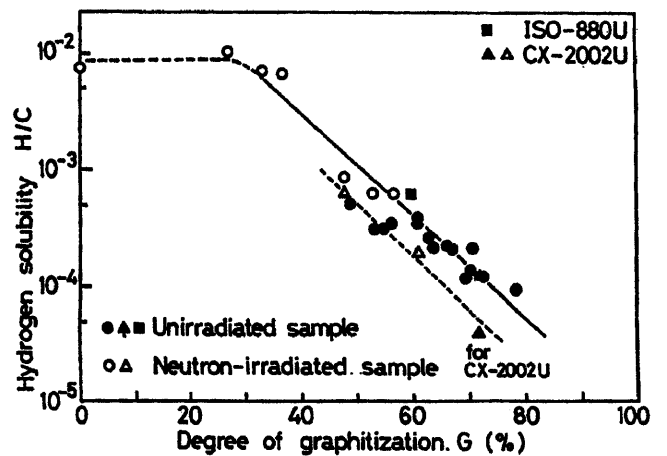

Fig.4. Correlation between hydrogen solubilities in graphite materials (isotropic graphites and CFCs, at 1273K under 101 kPa of H_2) and the degree of graphitization.

contention, hydrogen solubilities in graphite were plotted as a function of degree of graphitization. From Fig.4 one can see that the hydrogen solubility in graphite is strongly correlated to the degree of graphitization. The authors have reported that the increase of hydrogen solubility for CX-2002U after neutron irradiation was less than those for the isotropic graphites[2]. This can be explained well with the slight decrease of the degree of graphitization. Moreover, the hydrogen solubilities for both unirradiated and irradiated CX-2002U show nearly half amount of the values predicted from the correlation curve in Fig.4. This may be ascribed to the fact that either the carbon matrix or carbon fibers scarcely absorb hydrogen. Those samples showing the upward deviation from the correlation curve tend to have unsymmetrical peak in their X-ray diffraction

Table 1. Influence of irradiation temperature on hydrogen solubility in graphite (H/C ratios were normalized under one atmospheric pressure of hydrogen). Neutron irradiations were performed at a low temperature ($<$ 473K) and high temperature 873K) at the fluences of 1.9x 10^{24} n/m² and 6 x 10^{24} n/m², respectively.

sample	unirradiated	irradiated($<$ 200℃)	irradiated (600℃)
IG–110U	1.38 x 10^{-4}	6.69 x 10^{-3}	2.69 x 10^{-3}
IG–430U	2.13 x 10^{-4}	7.37 x 10^{-3}	3.73 x 10^{-3}

patterns. Since some graphites with high density are manufactured with different components and/or filling up technique into open pores, it sometimes make an unsymmetrical shape in diffraction peaks or corresponding lower degree of graphitization. For instance, the (002) diffraction peak for ISO-880U at 26.542 degree (2θ) had more gradual decay to lower angle side than higher one. And it can be decomposed into two components with the diffraction peaks at 26.1 and 26.542 degrees, although the height of the former peak is approximately equal to a quarter of the higher peak (26.542 degree). The former component corresponds to the degree of graphitization of only 16%. Such lower graphitized part in graphite should make the hydrogen solubility be larger than the value expected from the lattice spacing along c-axis which was determined simply from the peak angle of X-ray diffraction patterns.

### 3.3. Hydrogen retention and transport in graphite

From the observations that : 1) Hydrogen solubility in graphite at a given temperature increased with the reduction of the degree of graphitization and 2) Neutron irradiation enhanced hydrogen solubilty, the hydrogen solubility determined here must not be the true solubility in a crystalline graphite. A low degree of the graphitization (i.e. large lattice spacing of d_{002}) means the existence of not fully graphitized carbon atoms, i.e. dangling carbon bonds and/or defects. Hence, the hydrogen dissolution is most likely to be the trapping at the defect sites such as hydrogen trapping during ion implantation[7-9].

It is well-known that hydrogen implantation results in huge amount of hydrogen trapping up to an H/C ratio of 0.4[10].

The influence of the irradiation temperature on hydrogen solubility was also examined in this study, and the results are given in Table 1. The samples irradiated at higher temperature showed a lower hydrogen solubility. Similar observation has been reported by Causey et al.[11]. According to Niwase et al.[12,13], the defect density produced by the ion irradiation decreases with temperature, and amorphization does not take place above 773K even if the irradiation exceeds a damage level of 10 dpa. This is also consistent with some data from Maruyama et al.[14] showing that the thermal conductivity does not decrease much by neutron irradiation for the samples irradiated at higher

temperatures (e.g. 673K) as compared with that for room temperature.

If the hydrogen dissolution is mostly controlled by the hydrogen trapping at the defects, the following equilibria could be established between the defects (hydrogen trapping sites) and molecular hydrogen in a graphite grain,

H_2 2H (transient state) (2)

C* + H C-H , (3)
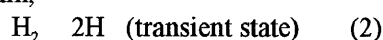
where C* is a trapping site for hydrogen. When the equilibrium constants k_1 and k_2 are given for the reactions of eqs.(2) and (3), respectively, the concentration of the trapped hydrogen (the solubility) can be expressed by

$$[C\text{-}H] = \sqrt{k_1} \bullet k_2 \bullet [C*] \bullet [H_2]^{1/2} \quad (4)$$

where [C*] and [H_2] are the concentration of vacant trapping sites and hydrogen molecules in a grain, respectively. Since the number of hydrogen molecules penetrating into the graphite grains should be proportional to hydrogen pressure[1], the hydrogen concentration in the graphite grain, [H_2], can be replaced with $\alpha \bullet P_{H2}$, where α is a proportional constant. The total concentration of trapping sites existing in the graphite grain, [C-H]+[C*], should be a intrinsic characteristic value for each sample. Then the hydrogen solubility will be

$$[C\text{-}H] = \frac{k_1 \bullet \sqrt{P_{H2}}}{1 \pm k_0 \bullet \sqrt{P_{H2}}} \bullet N_0 \quad (5)$$

where K_0 is a constant (the product of $k_1^{1/2}$, k_2 and α) and N_0 is the total concentration of the trapping sites. Thus, eqs.(4) and (5) suggest that the hydrogen solubility obeys the Sieverts' law when the concentration of vacant trapping sites [C*] is enough larger than that of [C-H]. It corresponds to the hydrogen solubility measurements under a low hydrogen pressure (eq.(5)), e.g. below 30 kPa in this study. When the hydrogen dissolution into graphite is controlled by the above reactions, the equilibrium reaction constant for the series of eqs.(2) and (3), $k_1^{1/2} \bullet k_2$, can be derived from the formula ΔG = -RT$\bullet$ln k with the activation energy for hydrogen dissolution into graphite (ΔG= -11.1 kJ/mol, Temperature range:973-1323K, Sample: ISO-880U)[3]. It becomes, for instance, 3.94 and 2.85 at 973K and 1273K, respectively. This equilibrium model was applied for the hydrogen solubility estimation obtained from deuterium desorption measurements with a quadrupole mass spectrometer, and the result is given in
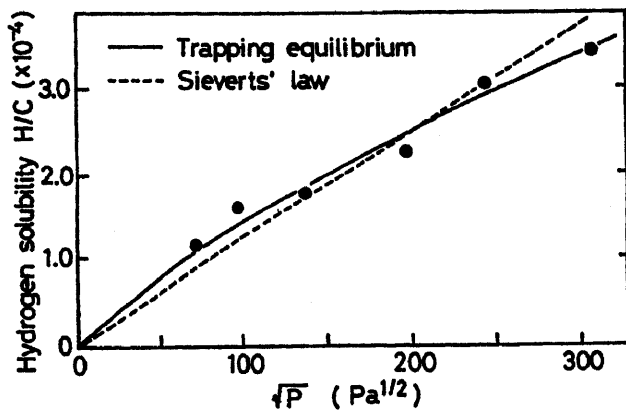
Fig.5. Pressure dependence of hydrogen solubilities in ISO-88 graphite exposed   to deuterium gas at 973K and the corresponding estimate using a trapping equilibrium hypothesis.

Fig.5. Then the ratio of hydrogen occupation in the trapping sites would be 34.7% at one atmospheric pressure of hydrogen (corresponding to the right end of the solid curve in Fig.5). This equilibrium reaction would be better representative in the pressure range of 1-100 kPa rather than the hydrogen chemisorption mechanism proposed by Gorodetsky et al.[9], since the chemisorption at 973K would not reproduce the pressure dependence such as shown in Fig.5.

Once the dissolution of hydrogen in graphites and CFCs can be interpreted as a trapping process, hydrogen transport in graphite should result from a sequence of detrapping and retrapping events with high energy activation processes, even if the transport appeared to be a diffusion-controlled process. This corresponds well to the fact that lower activation energies were observed in the diffusion measurements at hydrogen saturated region in graphite (vacant trapping sites are wholly filled up by hydrogen)[15,16] and, in contrast, the diffusion measurements with lower hydrogen concentration (vacant trapping sites are effective) gave higher activation energies (e.g. 1)).

4. Conclusions

The hydrogen dissolution phenomena and their relation to the graphitization characteristics of graphites and CFCs have been studied. The results are summarized as follows.
(1) Hydrogen solubilities in unirradiated graphite materials varied substantially (up to 16 times) among the eighteen samples investigated.
(2) A strong correlation has been recognized by the authors between hydrogen solubility and the degree of graphitization determined by X-ray diffraction technique. The sample with a higher degree of graphitization must have the less hydrogen solubility.

(3) Neutron irradiation enhances the hydrogen solubility and the enhancement is less for the higher temperature irradiation. This is attributed to the defect formation as a hydrogen trapping sites.
(4) Assuming the hydrogen dissolution into graphites and CFCs being as the hydrogen trapping at defects (such as dangling carbon bonds) in graphite, the hydrogen dissolution process can be explained well with an equilibrium reaction between hydrogen molecules and the trapping sites.
(5) Since hydrogen transport in graphites and CFCs is mainly controlled by trapping and detrapping, reported diffusion coefficients determined at lower hydrogen concentration should be strongly influenced by trapping effects.

1) H.Atsumi, S.Tokura and M.Miyake, J.Nucl.Mater. 155-157 (1988) 241.
2) H.Atsumi, M.Iseki and T.Shikama, J.Nucl.Mater. 191-194 (1992) 368.
3) H.Atsumi, M.Iseki and T.Shikama, J.Fac.Sci.Technol.Kinki University 27 (1991) 247.
4) H.Atsumi, M.Iseki and T.Shikama, in: Proceedings of Japan-CIS Workshop on   Interaction of Fuel Particles with Fusion Materials, Tokyo, 1992.
5) T.Yamashina, Ed. Overall Characterization of Graphites as Fusion First
    Wall Material and Evaluation of the Stability against Plasmas (Hokkaido
    University, Sapporo, 1989).
6) R.E.Franklin, Acta Cryst. 4 (1951) 235.
7) D.B.Kuzminov et al., J.Nucl.Mater. 185 (1991) 123.
8) V.Kh.Alimov, A.E.Gorodetsky and A.P.Zakharov, J.Nucl.Mater. 186 (1991)
    27.
9) A.E.Gorodetsky et al., in: Proceedings of Japan-CIS Workshop on
    Interaction of Fuel Particles with Fusion Materials, Tokyo, 1992.
10) W.M ller, J.Nucl.Mater. 162-164 (1989) 138.
11) R.A.Causey et al., Fusion Technology 19 (1991) 1585.
12) K.Niwase et al., J.Nucl.Mater. 179-181 (1991) 214.
13) K.Niwase and T.Tanabe, J.Nucl.Mater. 179-181 (1991) 218.
14) T.Maruyama and M.Harayama, J.Nucl.Mater. 195 (1992) 44.
15) K.Morita, K.Ohtsuka and Y.Hasebe, J.Nucl.Mater. 162-164 (1989) 990.
16) T.Tanabe and Y.Watanabe, J.Nucl.Mater. 179-181 (1991) 231.