Title	Desorption behavior of H2O from isotropic graphites dipped in water
Author(s)	Okita, Masao; Hirohata, Yuko; Hino, Tomoaki et al.
Citation	北海道大學工學部研究報告, 169, 69-76
Issue Date	1994-06-28
Doc URL	https://hdl.handle.net/2115/42421
Type	departmental bulletin paper
File Information	169_69-76.pdf

北海道大学工学部研究報告
第169号（平成6年）

Bulletin of the Faculty of Engineering
Hokkaido University No. 169 (1994)

Desorption behavior of H_2O from isotropic graphites dipped in water

Masao OKITA, Yuko HIROHATA, Tomoaki HINO and Toshiro YAMASHINA

(Received December 24, 1993)

Abstract

H_2O desorption behavior of isotropic graphites dipped in water was investigated by a technique of thermal desorption spectroscopy (TDS). Gas species, H_2, H_2O, CO, CO_2 and numerous hydrocarbons, were found to be desorbed from the graphite. The temperature with the maximum desorption rate of H_2O was around 873 K, for the ramp rate ranging from 0.083 to 0.83 K/s. The peak temperature of H_2O became again around 873 K, even after the heat treatment for the graphite sample at 625 K for 7 hrs prior to the TDS measurement. Apparent activation energy of the desorption for H_2O was obtained as 252 ± 24 kJ/mole. From the evaluation for value of the activation energy, it is presumed that the H_2O desorb due to the recombination between $-H$ and $-OH$ groups adsorbed on edge surfaces of the graphite.

1. INTRODUCTION

Graphite, because of its low atomic number, low vapor pressure and high thermal shock resistance, has been widely used for first wall protective tiles and limiter in the entire inner wall of the present-day nuclear fusion devices [1−7]. In particular, the isotropic graphite with isotropic properties on electrical resistance and thermal conductivity, has been often employed as first wall materials. Performance of fusion plasma confinement was remarkably improved by using the graphite material, because of the low radiation loss power [8].

However, it was reported that impurities such as oxygen and carbon in a plasma increased in stead of metal impurities, because of the gas desorption from the very porous structure [9−12]. Since the first wall material is often exposed in air in the case of the maintenance, the element gases of air, such as CO_2, H_2O and O_2, can easily adsorb on the graphite. The oxide formed on the graphite surfaces desorbs mainly in the form of CO and CO_2 due to the thermal and plasma irradiation during the plasma discharge shot. Then, the emitted CO and CO_2 dissociate to energetic ions or neutral species in the plasma. These species again bombard the graphite wall and sputter the carbons. The erosion yield of carbon due to energetic oxygen atom or ion is extremely high [13]. Therefore, the graphite wall is largely eroded by these processes. Thus, elucidation of desorption behavior of graphite after air exposure is a very important issue for the application to fusion devices. In

---

Department of Nuclear Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan

numerous studies, examined were the desorption behavior such as the amount of desorbed gases [14−21] and adsorbed gases [15,16,17,20]. It is well known that H_2O molecules reversibly bound to the carbon surface and desorb at low temperature [22,23]. Recently, it is reported that H_2O desorbs from graphite tiles exposed in air during long time period at a considerable high temperature [14,17,24]. However, the desorption behavior of H_2O emitted at such high temperature has not been systematically studied.

In a process of H_2O-desorption, it is not clarified yet either the H_2O desorbs by the surface reaction due to the recombination between -H and -OH groups or by the diffusion process of physically adsorbed H_2O molecules through micro pores. So, in this study, we investigated the desorption characteristics of H_2O emitted at the high temperature, such as activation energy for H_2O-desorption. For this purpose, the isotropic graphite dipped in water for a long time period was employed. We used a TDS technique [25,26] to evaluate the apparent activation energy and the amount of desorbed H_2O molecules. In addition, the effective surface area was measured by using a gas adsorption method to estimate the coverage of gases adsorbed on the graphite surface.

2. EXPERIMENTAL

A TDS vacuum system used in this work is shown schematically in Fig. 1. The system was evacuated both by a turbo molecular pump (TMP) and a Ti-sublimation pump. An orifice with diameter of 10 mm was attached between the vacuum chamber and the pumping system. In this pumping system, a base pressure of 3×10^{-7} Pa was achieved after bakeout at 443 K for 12 hrs. During the measurement of the thermal desorption spectrum, the chamber was evacuated only by the TMP. Thermally desorbed gases were analyzed by a quadrupole mass spectrometer (QMS), for the mass range from 2 amu to 45 amu. The change of total pressure was continuously monitored by using a Bayard-Alpert ionization gauge (BA).

The graphite sample was placed on a Ta-heater with resistive heating. The temperature was measured by a chromel-alumel thermocouple spot-welded to the heater. Before the TDS measurement for the graphite sample, only the Ta-heater was heated up to 1273 K, to obtain the TDS spectrum of a background level. The temperature ramp rate was adjusted by changing a current of power supply controlled with a PID controller. The temperature of the Ta-heater was linearly increased, i.e., $T=T_0+\beta t$. Here, β is the ramp rate which was changed from 0.083 to 0.83 K/s.

An isotropic graphite, fine grain graphite (IG-110U), supplied by Toyo Tanso Co., Inc. was employed as the sample. The apparent density, average pore diameter and pore volume of IG-11OU are 1.77 g/cm^3, 3 μm and 14−18 volume percents, respectively. A graphite sheet with a thickness of 1 mm was cut into the size of $10\times10\times1$ mm. The sample was treated in the following way : (1) degassed under UHV at 1273 K for 30 min in the TDS apparatus, (2) taken out from chamber and placed in atmosphere, (3) immediately dipped into water and hold for two days, (4) taken out from the water and immediately placed into the sample

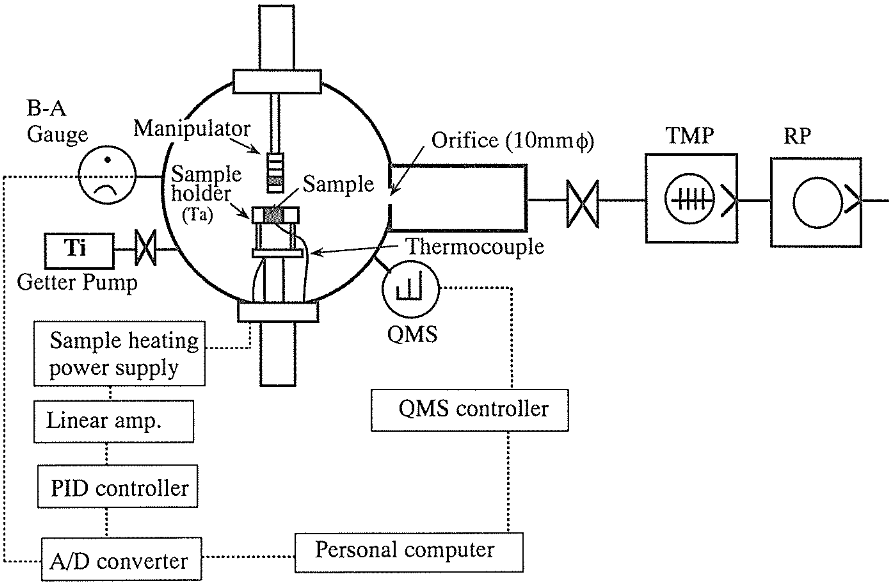

Fig. 1 Schematic diagram of experimental apparatus

holder, and (5) the chamber was pumped out. After this treatment, the TDS chamber was baked at 373 K, and then the sample was heated at the temperature lower than this baking temperature.

Before the above experiment, we also measured the desorption spectra of H_2O from the isotropic graphites dipped into the water for only 5 min and exposed to air for two days. The amount of H_2O desorbed from the wetted sample was approximately twice larger than that of the air exposed sample [15]. Thus, it is presumed that a large quantity of water is adsorbed on the graphite surface, because it is dipped into water for two days.

Surface area of IG-110U was measured by using a surface area measurement apparatus. The details of this apparatus are reported elsewhere [27]. In order to obtain adsorption isotherms, physical adsorption of xenon at liquid nitrogen temperature was utilized. Before the adsorption measurement, IG-110U was degassed at 573 K for one day under a pressure of about 1×10^{-5} Pa.

3. RESULTS AND DISCUSSION

(1) Desorbed gas species and the desorption temperatures

A typical TDS spectrum of isotropic graphite dipped in water is shown in Fig. 2. After the subtraction of the background level, all signal intensities were presented. Major thermally desorbed gas species were H_2, H_2O, CO and CO_2. These desorption spectra show that the temperature with the maximum desorption rate (T_p), is around 873 K, except H_2. Numerous hydrocarbons were also observed in the spectra. The signal intensities of hydrocarbons were one or two orders of magnitude smaller than those of the others. The peak temperatures of hydrocarbons were observed around 980 K, close to that of H_2. Figure 3 shows a mass spectrum when the sample temperature was about 880 K. Cracking ions of masses which correspond to C_1, C_2, C_3 and C_4 hydrocarbons [28], were clearly observed. If the QMS is widely scanned to a higher range, other hydrocarbons ($> C_4$) [29] might be observed.

In the present TDS apparatus, it is possible to admit the H_2O vapor through the variable leak valve from the reservoir. So, the thermal desorption spectrum from the graphite sample exposed to H_2O vapor was also studied. Although the sample had been contacted with the H_2O vapor at the exposure level up to 1×10^7 L, peak temperature of H_2O-desorption was not observed around 873K. It was reported by Fukui et.al. [30] that the desorption peak

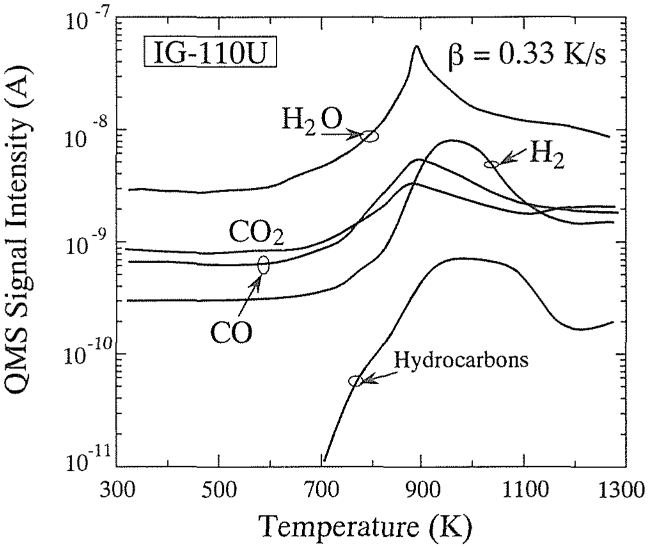

Fig. 2 Typical TDS spectrum of isotropic graphite after dipping in a water

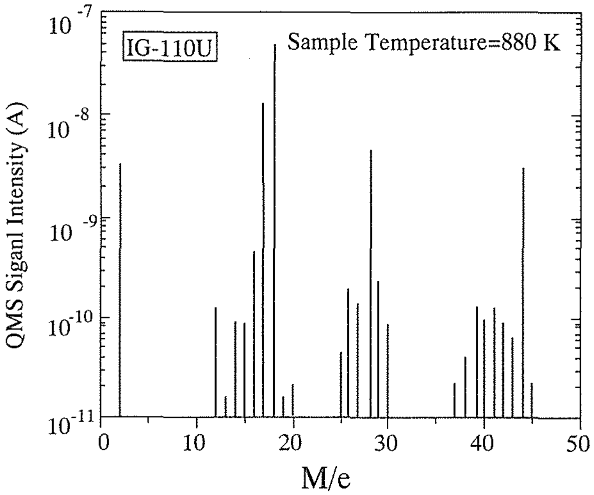

Fig. 3 Mass spectrum of isotropic graphite

of H_2O was not observed from graphite film made on nickel after H_2O exposure at 570 L, but peak temperature of H_2O was observed around 500 K after air exposure for one day. These results suggest that the H_2O desorption at the high temperature considerably depends on the exposure level.

(2) Activation energy of the desorption

The activation energy of the desorption (E_d) is estimated from the TDS spectra taken with different ramp rates. Figure 4 shows the plot of ln (T_p^2/β) against $1/T_p$ for H_2O, CO, CO_2 and H_2. The linearity between ln (T_p^2/β) and $1/T_p$ was found in the figure. If these gases desorb due to either first-order reactions or second-order reactions, the activation energy, E_d, can be evaluated from the slope of the straight line [25]. The activation energies of desorption for CO, CO_2 and H_2 were obtained as 235±20, 212±10 kJ/mole and 95±14 kJ/mole, respectively. The values of E_d for CO and CO_2 agree with those reported by Marchon et.al, [29]. They concluded that a lactone group and a semiquinone group were precursors of CO_2 and CO, respectively. Although T_p of H_2 was higher than those of the others, the value of E_d became small.

The activation energy of H_2O was obtained as 252±24 kJ/mole. The present value was larger than those reported, e.g., the heat of condensation of H_2O (= 55 kJ/mole) and E_d of of H_2O-desorption from graphite films (= 11.5–35.6 kJ/mole) [23] and the binding energy between a H_2O molecule and edge carbon atoms of graphite powder (= 146 kJ/mole) [29]. The present value was rather close to the heat of H_2O formation ($H_2+1/2\ O_2 \longrightarrow H_2O : \Delta H = -242$ kJ/mole).

On the other hand, the activation energy due to diffusion of physically adsorbed H_2O molecules through micro pores has been estimated as 22.6 and 38.1 kJ/mole (25–75 °C) [32]. Sevenster also measured the activation energy of diffusion, E_D, and diffusion constant (D_o) of H_2O in a coal as 8.8–11.7 kJ/mole, (4.8–6.4)× 10^{-13} cm^2/s, respectively at low temperature region (25–60 °C) [33]. The activation energy obtained in the present study was also larger than that of the diffusion process.

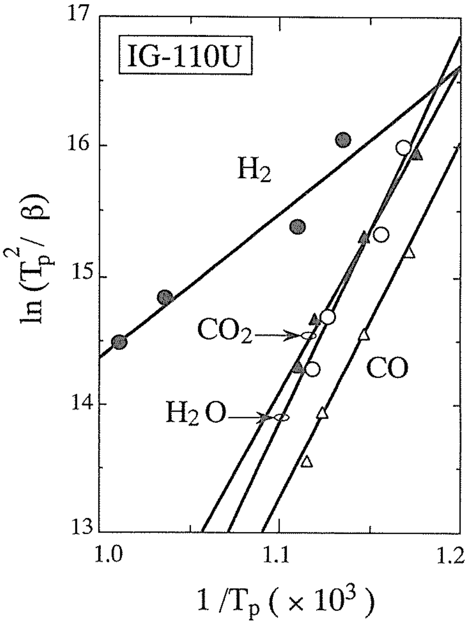

Fig. 4 Reciprocal peak temperature (T_p) versus ln (T_p^2/β)

(3) TDS spectra of H_2O after preheating

We examined the TDS spectra for the sample preheated with different heating condition, prior to the TDS measurement. After the heat treatment, the sample temperature was continuously risen up to 1273 K with 0.17 K/s. The TDS spectra of H_2O are shown in Fig. 5. The TDS spectrum of preheated sample for 7 hrs at 623 K, was very similar to that for 1 hr. The peak temperatures were observed again at the high temperature close to 870 K. Dubinin reported [22] that most of adsorbed water was removed by only evacuating the active carbon at 20 °C. The residual quantity, however, could not be desorbed by only evacuating, after the carbon sample was left more than several months. In order to desorb most of the residual quantity, the heating at the temperature of 623 K was needed in the experiment of Dubinin.

Even if samples were preheated at 723 K and 773 K for 2 hrs, the desorption peaks were also observed at around 850 K. Therefore, if isotropic graphite has a lot of maicro pores, H_2O molecules physically adsorbed on the carbon atoms of intersurface of micro pores might be already desorbed during these preheating.

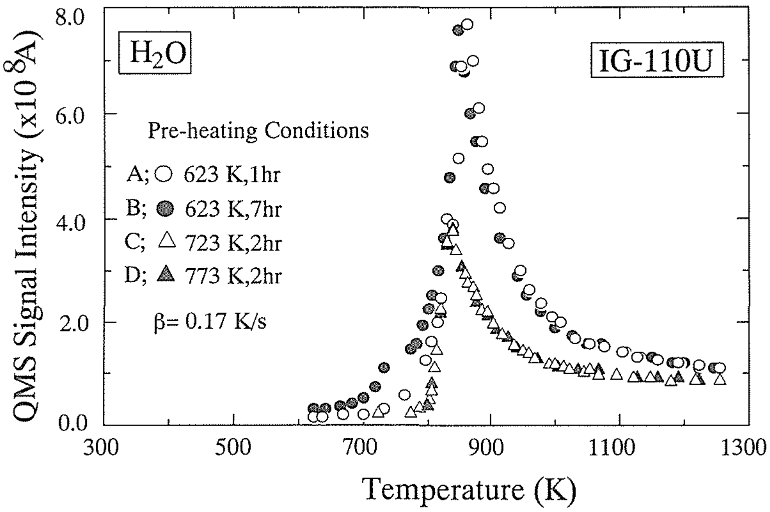

Fig. 5 H_2O desorption spectra after preheating of wetted sample

(4) TDS spectra of H_2O for samples with different thickness

Figure 6 shows TDS spectra of H_2O desorbed from IG-110U with different thickness. In these curves, the background level was not subtracted. If H_2O desorbs due to diffusion process, the peak temperature might be shift to lower temperature with decrease of thickness. However, all of the peak temperatures were observed around 870 K. This result supports the previous conclusion, e.g., the recombination between -H and -OH groups adsorbed on the edge surfaces of graphite occurs around the peak temperature.

Tremblay et.al, reported that phenol (hydroxyl), hydroquinone, aldehyde and carboxylic acid are regarded as the function groups produced a H_2O molecules [34]. Yamabe and Takahashi proposed that H_2O is produced from -COOH groups and -OH groups [35]. Kelemen [36], Marchon [29] and Herman and Huttinger [37] proposed that -OH or ether

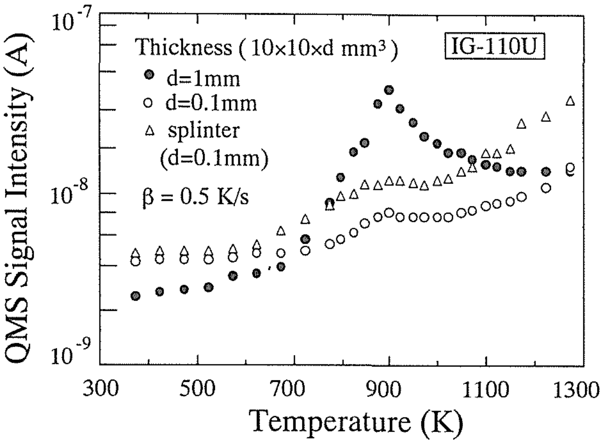

Fig. 6 TDS spectra of H_2O desorption of wetted graphite with different thickness

groups exist on graphite or active carbon surface after wetting. However, Smith and coauthors reported that phenolic -OH bond remained on the graphite surface after heating at a temperature of 953 K [38]. So we guessed that H_2O molecules are desorbed at high temperature due to the recombination between C-H group and hydroxylic -OH group on the graphite surface.

The total amount of the desorption for H_2O molecules was estimated by using pumping speed and sensitivity of QMS of H_2O as $(1.5-4.0)\times10^{17}$ molecules/g. Since surface area of IG-110U was obtained as 0.7 m^2/g, surface density of carbon atoms was roughly estimated as 2×10^{19} atoms/m^2. From the value of desorption amount and surface density of carbon atoms, the coverage of precursors of H_2O is estimated from 0.01 to 0.025, when H_2O desorbs due to the recombination between a -H and a -OH group.

4. SUMMARY

We investigated the desorption of H_2O observed at high temperature. There were two possibilities, i.e., the surface reaction due to the recombination between -H and -OH groups or the diffusion process of physically adsorbed H_2O molecules through micro pores. The apparent activation energy for H_2O emitted around at 873 K was obtained as 252+24 kJ/mole. From the value of activation energy and dependences of peak temperatures on thickness and preheating condition, it was presumed that H_2O dissociatively adsorbed on edge surfaces of the graphite and desorbed due to the recombination between C-H and hydroxylic -OH groups.

Acknowledgments

The authors acknowledge Toyo Tanso Co., Inc. for the supply of IG-110U samples.

References

1. K.J. Dietz ; J. Nucl. Mater., 155−157 8 (1988)
2. R.H. Rebut, K.J. Dietz and P.P. Lallia ; J. Nucl. Mater., 162−164 172 (1989)
3. H. Takasu and the JT-60 team : J. Nucl. Mater., 155−157 27 (1988)
4. N. Hosogaya and the JT-60 team : J. Nucl. Mater., 162−164 93 (1989)
5. H.F. Dylla et.al. ; J. Nucl. Mater., 155−157 15 (1988) and 162−164 128 (1989)
6. U. Samm et.al. ; J. Nucl. Mater., 162−164 24 (1989)
7. G. Fussmann and the NET team ; J. Nucl. Mater., 162−164 14 (1989)
8. T. Yamashina and T. Hino ; Appl. Surf. Sci., 48−49 483 (1991)
9. M. Ulrickson, the JET team and the TFTR team ; J. Nucl. Mater., 176−177 44 (1990)
10. J. Winter ; J. Nucl. Mater., 176−177 14 (1990)
11. H.A. Claassen, R.P. Schorn, H. Geerhauser and E. Hintz ; J. Nucl. Mater., 176−177 398 (1990)
12. P.R. Thomas and the JET team ; J. Nucl. Mater., 176−177 3 (1990)
13. E. Vietzke, T. Tanabe, V. Philipps, M. Erdweg and K. Flaskamp ; J. Nucl.Mater. 145−147 425 (1987)
14. Y. Hirohata, S. Fukuda, T. Hino and T. Yamashina ; Bull. Fac. Eng. of Hokkaido Univ., No. 140 167 (1988)
15. Y. Hirohata, T. Yanagisawa, Y. Nakayama, T. Hino and T. Yamashina ; J. Vac. Soc. Japan, 33 209 (1990)
16. Y. Kubota and A. Miyahara ; Report of IPP of Nagoya Univ., IPPJ-DT-139 (1988)
17. A.E. Pontau and D.H. Morse ; J. Nucl. Mater., 141−143 124 (1986)
18. J. Bohdansky, R.A. Causey, C.D. Croessmann, A.E. Pontau and J.B. Whitley ; J. Nucl. Mater., 162−164 861 (1989)
19. Y. Watanabe T. Tanabe and S. Imoto ; Fusion Eng. and Design, 9 143 (1989)
20. Y. Kubota, K. Akaishi, M. Asano and S. Watanabe ; J. Vac. Soc. Japan, 33 337 (1990)
21. H. Vernikel et.al. ; Report of Max- Planck-Institute fur Plasmaphysik 1/239 (1987)
22. M.M. Dubinin ; "Chemistry and Physics of Carbon" vol. 2 Marcel Dekker Inc. New York, p111−118 (1988)
23. S. Kato, H. Oyama and H. Odagiri ; Vacuum 41 1998 (1990)
24. J. Bohdansky et.al. ; Instruments and Methods in Physics Reserch B23 527 (1987)
25. P. Redhead ; Vacuum, 12 203 (1962)
26. G. Carter ; Vacuum 12 245 (1962)
27. K. Watanabe and T. Yamashina ; Vacuum, 22 183 (1972)
28. Y. Nakayama, S. Fukuda and T. Yamashina ; J. Vac. Soc. Japan, 32 415 (1989)
29. B. Marchon, J. Carrazza, H. Heinemann and G.A. Somorjai ; Carbon 26 507 (1988)
30. J. Fukui, D. Fujita and T. Homma ; J. Vac. Soc. Japan, 33 333 (1990)
31. D. Fujita, T. Homma, N. Tanaka and T. Sato ; J. Vac. Soc. Japan, 31 525 (1988)
32. A. Tiselius ; Z. Physik. Chem., 169A 425 (1934) and 174A 401 (1935)
33. P.G. Sevenster ; Fuel 38 403 (1959)
34. G. Tremblay, F.J. Vastola and P.L. Walker. Jr. ;Carbon 16 35 (1978)
35. K. Yamabe and H. Takahashi ; Tanso No. 120 106 (1980)
37. S.R. Kelemen, H. Freund and C.A. Mims ; J. Vac. Sci. Technol., A2 987 (1984)
37. G. Hermann and K. Huttinger ; Carbon 24 705 (1986)
38. R.N. Smith, D.A. Young and R.A. Smith ; Trans Farad. Soc. 62 1034 (1966)