ELSEVIER

Journal of Nuclear Materials 241–243 (1997) 1060–1064

journal of nuclear materials

Release of hydrogen from co-existing layers of carbon and beryllium with vacuum heating

Kan Ashida [a,*], Kuniaki Watanabe [a], Toshio Okabe [b]

[a] Hydrogen Isotope Research Center, Toyama University, Gofuku 3190, Toyama 930, Japan
[b] Department of Physics, Faculty of Science, Toyama University, Gofuku 3190, Toyama 930, Japan

Abstract

Carbon films containing hydrogen were prepared on quartz and Be plates by means of a plasma discharge in C_2H_4. Raman spectroscopy revealed that the carbon film on quartz was stable to heating in vacuo up to 800°C. On the other hand, X-ray diffraction measurements of the film prepared on the Be plates revealed that Be_2C was formed above 500°C. The intensity of the Be_2C peak increased with increasing temperature. Thermal desorption spectroscopy showed that hydrogen molecules were desorbed from the carbon films containing hydrogen by two different mechanisms. One is the reaction of C and adsorbed water to form H_2 and CO at around 400°C, and the other is the reaction of C and Be to form H_2 and Be_2C above 500°C.

Keywords: Carbon; Beryllium; Surface layer; Fuel recycling and inventory

1. Introduction

To reduce the radiation loss of a burning plasma, low Z substances are being applied as plasma facing material (PFM). At present, beryllium (Be) and carbon (C) are used in large experimental devices such as the joint european torus (JET) [1,2]. These materials are also identified as candidates of PFM for the international thermonuclear experimental reactor (ITER) [3,4]. In the devices, PFM will be bombarded and heated up to high temperatures by high fluences of energetic hydrogen isotope ions and neutrals. Physical and chemical sputtering causes erosion of PFM and impurity release into the plasma. They will subsequently be deposited back onto the wall surface and form layers containing the elements of all materials used at the vessel wall [1,5]. Because the nature of such layers is anticipated to differ from each material [6,7], it is important to understand the physicochemical properties of these layers such as consisting of Be and C with respect to fuel recycling, inventory and so on. A large amount of hydrogen was found to accumulate as carbonaceous deposits owing to the formation of stable chemical bonds between carbon and hydrogen isotopes. Accordingly, the release behavior of hydrogen isotopes from such layers as well as each of the materials should be investigated to control the fuel recycling and inventory.

In this study, carbon films containing hydrogen were prepared on Be plates as a model of the co-existing system of Be and C. Changes in physicochemical properties of the surface layers with heating in vacuo were measured by means of Raman spectroscopy (RS) and X-ray diffractometry (XRD) along with mass analyzed thermal desorption spectroscopy (TDS). In the present paper, the release behavior of hydrogen from such a layer is discussed on the basis of changes in crystallographic structure and chemical reactions due to heating in vacuo.

2. Experimental

2.1. Sample preparation

Carbon films containing hydrogen were prepared by rf discharge of C_2H_4. One carbon film was deposited on a quartz plate ($10 \times 10 \times 0.5$ mm), denoted as [C/Qz], and the other was a film on a Be plate of similar size (denoted

---

[*] Corresponding author. Tel.: +81-764 45 6927; fax: +81-764 45 6931; e-mail: ashida@hrc.toyama-u.ac.jp.

PII S0022-3115(96)00660-5

as [C/Be]), the latter being used to simulate a co-existing system of Be and C. The beryllium used was the hot-pressed plate of reactor grade purchased from NGK Insulators. Its density and size were 1.85 g/cm^3 and $10 \times 10 \times 0.5$ mm, respectively. The purity was guaranteed as above 99.8%, where BeO was the main impurity (0.46 mol%). The C_2H_4 gas was of pure grade (Sumitomo Seika) and used without further purification.

The quartz or the mechanically polished Be plates were put in a quartz tube of 15 mm diameter attached to a vacuum system, which was equipped with a quadrupole mass spectrometer (ULVAC MSQ-150A), a sputter-ion pump and a turbomolecular pump backed with an oil-sealed rotary pump. It could be evacuated below 7×10^{-8} Pa. After evacuation of the system below 1×10^{-7} Pa, C_2H_4 gas was introduced into the plasma chamber at a pressure of 40 Pa and an rf discharge was started. The frequency and the power applied for the discharge were 13.56 MHz and 40 W, respectively.

2.2. RS, XRD and TDS measurements

Raman spectroscopy (RS) and X-ray diffractometry (XRD) were used to characterize the surface states of the samples before and after heating in vacuo. After surface characterization of an as-deposited sample at room temperature, it was put into a quartz tube attached to the vacuum system for heating under given conditions. The sample could be heated up to 900°C, where the temperature was measured with a Pt/Pt–Rh (13%) thermocouple attached to the outside surface of the quartz tube. Subsequently, the sample was cooled to room temperature, and was removed in air for the RS and/or XRD measurements.

Raman spectra were measured using a JASCO laser Raman spectrometer, RFT-200. The probe was a YAG laser operated at 1064 nm with 400 mW power. The detection angle was normal to the sample surface, and the resolution was kept at 2 cm^{-1}. The number of signal iterations was set to 1000 in this study.

XRD was used to examine the crystallographic change in the surface layer of the [C/Be] sample. XRD patterns were recorded by an X-ray diffractometer, Phillips PW1700. The probe was the Cu Kα line operated at 0.1572 nm with 1200 W power. The incident angle of X-rays was fixed at 3° to the surface of the sample to observe a thin sub-surface layer.

The sample was heated linearly with time from room temperature to 800°C for thermal desorption spectroscopy (TDS). The heating rate was 9.8 K/min. The partial pressures of desorbing gases were measured with a quadrupole mass spectrometer.

3. Results

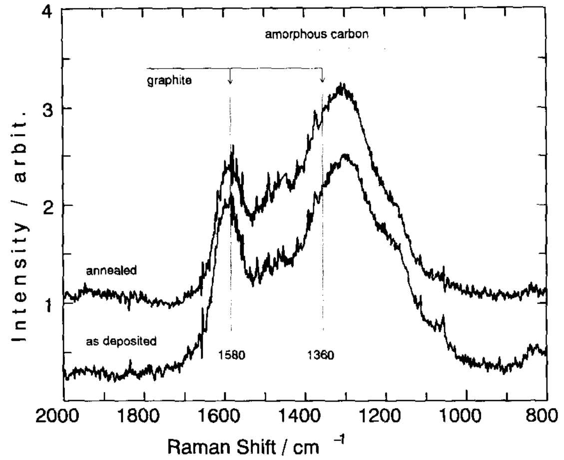

Fig. 1. Raman spectra for a [C/Qz] sample before (lower) and after (upper) vacuum heating at 800°C for 10 min.

Fig. 1 shows the Raman spectra observed for the [C/Qz] sample before (lower) and after (upper) heating in vacuo at 800°C for 10 min. The as-deposited [C/Qz] sample showed a broad band at around 1300 cm^{-1} and a relatively narrow band at about 1600 cm^{-1}. It is seen in the figure that the vacuum heating caused no significant change in [C/Qz] film.

Fig. 2 shows the XRD patterns for the [C/Be] sample after vacuum heating for 10 min at given temperatures. This figure shows that no diffraction peak relating to carbon appeared with heating below 400°C. The observed peaks were attributed to metallic Be and its oxide. On the other hand, new diffraction peaks at $2\theta = 36$ and 60° were observed above 500°C and assigned to beryllium carbide. This indicates that Be_2C was formed in the sub-surface layer of the sample. The intensities of these peaks in-

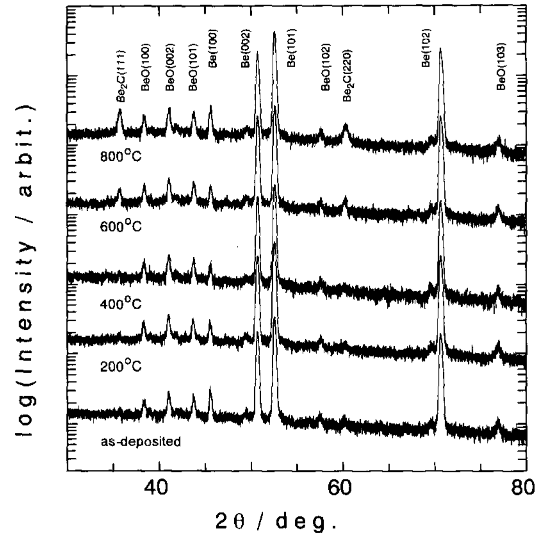

Fig. 2. Variation of XRD patterns for the [C/Be] sample with vacuum heating for 10 min at given temperatures.

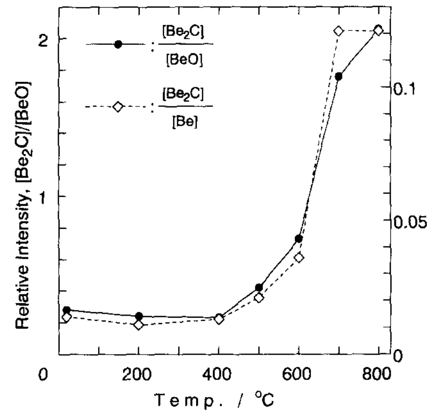

Fig. 3. Change in the relative intensities of $Be_2C(111)$ peak with vacuum heating at given temperatures.

creased with increasing temperature. Fig. 3 shows changes in the relative intensities of $Be_2C(111)$ peak with temperature. They are normalized by the intensities of Be(101) and BeO(002) peaks regarded as internal standards. From this figure, the relative intensities of Be_2C remained at a noise level below 500°C, whereas they sharply increased with increasing temperature to reach a constant value above 700°C.

Fig. 4(a) shows the TDS spectra of main desorption gases from a quartz plate and the quartz tube which was designed for TDS measurements. The signal intensities were kept at almost background levels, but small peaks appeared for $M/e = 18$ and 28 at around 300°C. Similar results were obtained for the bare Be plate. Fig. 4(b) shows the TDS spectra for the [C/Qz] sample. Desorption peaks of $M/e = 2$ and 28 appeared at around 400°C along with a small peak of $M/e = 16$. Fig. 4(c) shows the TDS spectra for the [C/Be] sample. Desorption peaks of $M/e = 2$ and 28 were observed at around 400°C with a small peak of $M/e = 16$. The most intense peak of $M/e = 2$, however, was observed above 500°C, indicating that the majority of the hydrogen atoms in the film was released in a higher temperature region. The analyses of fragment peaks strongly suggested the peaks of $M/e = 2$, 16, 18 and 28 were due to H_2^+ CH_4^+, H_2O^+ and CO^+, respectively.

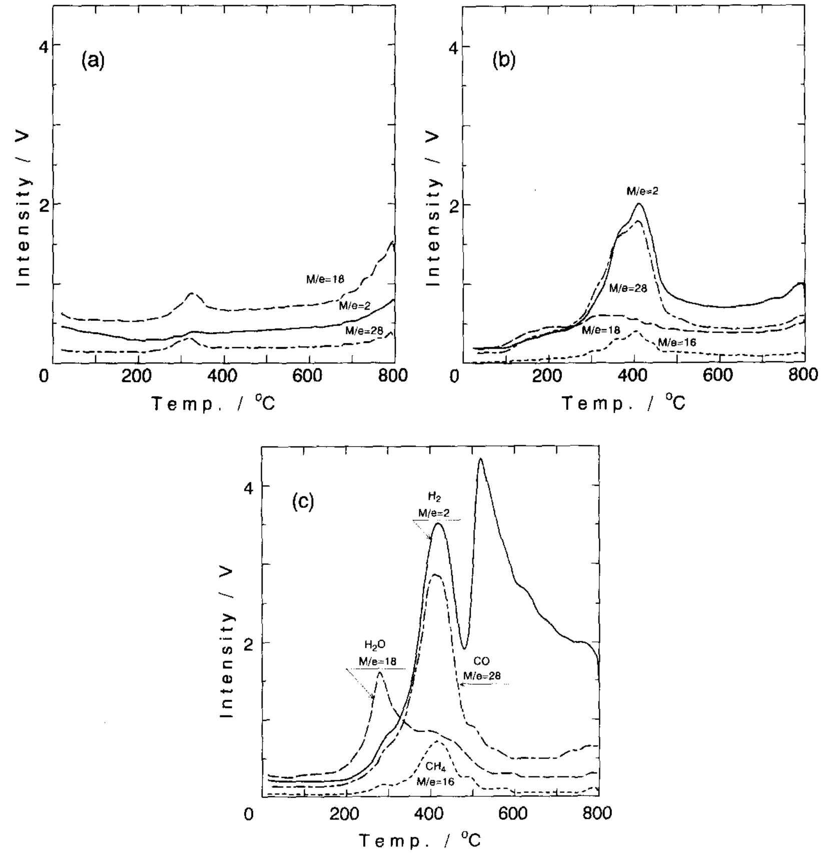

Fig. 4. TDS spectra of main desorption gases from (a) quartz plate and quartz tube which was designed only for the TDS measurements, (b) quartz plate covered with carbon film containing hydrogen ([C/Qz] sample), (c) beryllium plate covered with carbon film containing hydrogen ([C/Be] sample). Desorbed species were assigned as indicated in the figure.

4. Discussion

The principal features of the RS spectra of the [C/Qz] sample shown in Fig. 1 are quite analogous to those observed for an amorphous carbon (denoted as 'a-carbon') film [8–10]. The XRD measurements also showed that there was no crystalline phase of carbon in the deposited carbon film before and after vacuum heating (Fig. 2). Those observations clearly indicate that the a-carbon constitutes the principal part of the deposited carbonaceous film. In addition, the formation of some other carbon compounds was implied by the appearance of small shoulder bands at around 1200 and 1500 cm^{-1} in Fig. 1. The most relevant Raman bands arise around 1600 cm^{-1} from stretching vibrations of C=C bond as highly polarized bands [11]. Tibbitt et al. have also found various kinds of hydrocarbon residues containing a number of hydrogen atoms in high concentration by forming C–H bonds [12]. Various vibrational modes of CH, CH_2 and CH_3 are also expected in the range from 1100 to 1500 cm^{-1} [11]. Accordingly, it can be concluded that the carbonaceous film prepared in the present study mainly consists of a-carbon, where a large number of hydrogen atoms are captured by carbon atoms forming stable chemical bonds such as C–H. Consequently, they are hardly desorbed from the film by vacuum heating alone.

The layer of C on Be, however, readily reacts with H_2O and Be. Namely, water molecules react at relatively low temperature with carbon atoms in the matrix of the carbonaceous film to release hydrogen back into vacuum [13]. This appears also true for other impurity gases containing oxygen such as CO_2. This suggests that such impurity gases would enhance detrapping of hydrogen isotopes captured in carbonaceous deposits on the first wall of tokamak using carbon as PFM.

In addition to the mechanism mentioned above, captured hydrogen isotopes can be also released from the deposited carbonaceous film through the reaction between C and Be. This reaction is expected to proceed to completion not only on the surface, but also in the bulk of the C layer on Be.

Concerning the TDS peaks in the low temperature region below 500°C, the following reactions likely take place on both of the [C/Qz] and [C/Be] samples [13].

$$[\mathrm{CH}_n]_m + x\mathrm{H_2O} \rightarrow x\mathrm{C(O)} + (x + mn/2)\mathrm{H_2} \qquad (1)$$

$$\mathrm{C(O)} \rightarrow \mathrm{CO(g)}, \qquad (2)$$

where $[\mathrm{CH}_n]_m$ represents the carbon film containing hydrogen deposited from C_2H_4 plasma, H_2O a water molecule adsorbed on the sample surface exposed to air for RS and/or XRD measurements, and C(O) a site occupied by an adsorbed oxygen atom [13]. From the reaction scheme (Eq. (1)), the amount of desorbed H_2 is expected to be larger than that of CO because of the contribution of inherent hydrogen atoms in the deposited carbon film. In fact, the relative ionization cross-sections and mass-dependent sensitivity of the mass spectrometer for H_2 and CO being taken into account [14,15], the desorbed amount of H_2 is factor two or more larger than that of CO.

In comparison with the low temperature region, release of a larger amount of H_2 was observed for the [C/Be] sample in the high temperature region above 500°C. In contrast, no noticeable H_2 release was observed for the [C/Qz] sample in this temperature region. The temperature for hydrogen release was considerably lower than that observed for graphite [16,17]. The difference in the release temperatures indicates that the release mechanisms of hydrogen differ. Graphite shows three desorption peaks, denominated as [I], [II] and [III], in the desorption spectra [17]. The desorption peak [I], the lowest temperature peak, obeys second order kinetics, indicating that the rate determining step is the surface association reaction of trapped hydrogen atoms in graphite. Although the temperature of the desorption peak shifts with the concentration of hydrogen isotopes in graphite and temperature ramp, the desorption peak [I] does not fall below 600°C. Therefore, other mechanisms play a role in the appearance of the desorption peak of H_2 at 520°C. The XRD analysis revealed that Be_2C formation took place at the same temperature region. Those results indicate that the formation of Be_2C and associated desorption of H_2 takes place above 500°C as

$$[\mathrm{CH}_n]_m + 2\mathrm{Be} \rightarrow \mathrm{Be_2C} + (mn/2)\mathrm{H_2}, \qquad (3)$$

where Be represents beryllium atoms diffused to the surface from the bulk.

According to the previous secondary ion mass spectroscopic (SIMS) investigations [18], negative secondary ions, such as C^-, C_2^-, CH^-, and C_2H^-, were observed on the [C/Be] sample. This indicates that hydrogen isotope atoms are captured by carbon atoms on the sample surface. The SIMS measurements also showed evidence of Be_2C formation, which was confirmed by the presence of BeC^- ($M/e = 21$). Hydrogen atoms captured by Be_2C, however, were not found, suggesting that Be-carbide has little ability to capture/trap hydrogen isotope atoms. This is the reason that hydrogen was released to the gas phase as in Eq. (3).

The above mentioned facts suggest that hydrogen isotopes captured by carbonaceous deposits will be detrapped through the formation of Be_2C. Because this reaction is expected to proceed to completion by consuming almost all beryllium and/or carbon atoms in a co-existing system of C and Be, the inventory of fuel particles should decrease significantly. Eventually, considerable change should occur in the fuel recycling properties of the first wall because of the increase in Be_2C, which lacks the ability to capture fuel particles.

5. Conclusions

Changes in the physicochemical properties of the co-existing layers of Be and C with heating in vacuo were studied by means of Raman spectroscopy and X-ray diffractometry along with mass analyzed thermal desorption spectroscopy. The conclusions of the present study are summarized as follows:

(1) The carbonaceous layer prepared by means of a rf C_2H_4 discharge consists mainly of a-carbon, where a large number of hydrogen atoms are captured by carbon atoms forming stable chemical bonds as C–H. They are hardly desorbed from the film by heating in vacuo alone due to the strong bonding between carbon and hydrogen atoms.

(2) Water molecules react at relatively low temperature with carbon atoms in the matrix of the carbonaceous layer to release back hydrogen into vacuum. This fact suggests that impurity gases containing oxygen would enhance detrapping of hydrogen isotopes captured in the carbonaceous deposits on the first wall of tokamak using carbon as PFM.

(3) Hydrogen atoms can be also released from the co-existing layers of C and Be through the reaction between C and Be. This reaction is expected to proceed to completion not only at the surface, but also in the bulk of the co-existing layer of C and Be.

(4) Beryllium carbide, Be_2C, has only little ability to capture hydrogen isotopes and hence the tritium inventory is expected to become quite small in high temperature parts of the tokamak wall such as the divertor, in which C and Be are involved together as PFMs.

Acknowledgements

The authors thank to Professor K. Kanamori, Toyama University, for his helpful discussion and advice on RS measurements.

References

[1] R. Behrisch, A.P. Martinelli, S. Grigull, R. Grotzschel, U. Kreissig, D. Hildebrandt and W. Schneider, J. Nucl. Mater. 220–222 (1995) 590.

[2] E.B. Deksnis, H.D. Falter, A.T. Peacock, M.A. Pick and R. Viola, J. Nucl. Mater. 212–215 (1994) 1266.

[3] G. Janeschitz, K. Borrass, G. Federici, Y. Igitkhanov, A. Kukushkin, H.D. Pacher, G.W. Pacher and M. Sugihara, J. Nucl. Mater. 220–222 (1995) 73.

[4] R.A. Causey and K.L. Wilson, J. Nucl. Mater. 212–215 (1994) 1436.

[5] E. Hechtl, J. Roth, W. Eckstein and C.H. Wu, J. Nucl. Mater. 220–222 (1995) 883.

[6] A.P. Martinelli, R. Behrisch and A.T. Peacock, J. Nucl. Mater. 212–215 (1994) 1245.

[7] E.A. Denisov, T.N. Kompaniets, A.A. Kurdyumov, S.N. Mazayev and Yu.G. Prokofiev, J. Nucl. Mater. 212–215 (1994) 1448.

[8] R.O. Dillon, J.A. Woollam and V. Katkanant, Phys. Rev. B 29(6) (1984) 3482.

[9] K. Ashida, K. Kanamori, K. Ichimura, M. Matsuyama and K. Watanabe, J. Nucl. Mater. 137 (1986) 288.

[10] N. Wada, P.J. Gaczi and S.A. Solin, J. Non-Cryst. Solids 35–36 (1980) 543.

[11] F.R. Dollish, W.G. Fateley and F.F. Bentley, Characteristic Raman Frequencies of Organic Compounds (Wiley/Interscience, 1974).

[12] J.M. Tibbitt, A.T. Bell and M. Shen, eds., J. Macromol. Sci. Chem. A 11(1) (1977) 139.

[13] H. Marsh, ed., Introduction to Carbon Science (Butterworths, 1989).

[14] N.R. Reagan, L.C. Frees and J.W. Gray, J. Vac. Sci. Technol. A 5(4) (1987) 2389.

[15] R. Holand, J. Vac. Sci. Technol. 10(6) (1973) 1133.

[16] K. Ashida, K. Ichimura, M. Matsuyama and K. Watanabe, J. Nucl. Mater. 128–129 (1984) 792.

[17] K. Ashida, K. Ichimura, M. Matsuyama and K. Watanabe, Fusion Technol. 14 (1988) 735.

[18] K. Ashida, M. Matsuyama, K. Watanabe, H. Kawamura and E. Ishitsuka, J. Nucl. Mater. 210 (1994) 233.