

論 文

ベリリウム-炭素共存系の真空加熱による状態変化

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Changes in the Chemical States of Co-existing Layers of Beryllium and Carbon with Vacuum Heating

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(Received October 9, 1995 ; accepted December 22, 1995)

Abstract

The changes in the chemical states of co-existing layers of Be and C with vacuum heating were studied for two different samples using XPS and SIMS surface analysis techniques. One type of sample was a Be plate covered with evaporated C film, denoted as [C/Be], and the other Be implanted with ethylene ions, denoted as [C-Be]. It was found that Be₂C was formed by vacuum heating above 600°C on the [C/Be] sample. For the [C-Be] sample, however, a part of the surface Be was already changed to Be₂C by the ion implantation. In addition, SIMS measurements showed hydrogen relating secondary ions such as CX⁻, C₂X⁻, and OX⁻ (X=H and D), indicating that

C and O act as trapping sites of hydrogen isotopes on/in the co-existing layers of Be and C.

1. Introduction

Plasma material interactions (PMI) are important to confine high temperature plasma in controlled thermonuclear fusion devices. To understand the behavior of fuel particles in plasma facing materials (PFM), the change in the surface states of PFM under various conditions should be studied in detail as well as the mechanisms of trapping-detrapping processes of the fuel particles in these materials.

To reduce the radiation loss of burning plasma, attention has been paid to low-Z materials as PFM. At present, beryllium (Be) and carbon (C) are used for PFM in large experimental devices such as Joint European Torus (JET)^{1, 2}, and identified as candidates of PFM for International Thermonuclear Experimental Reactor (ITER)^{3, 4}. In such large devices, however, Be and C will be used together, and a co-existing layer of Be and C will be formed due to physical and/or chemical sputtering and so on¹⁻⁵. Therefore, physicochemical properties of the co-existing layers of Be and C is one of the important problems for fuel recycling, because the nature of such layers is anticipated to differ from each of the materials^{6, 7}. Accordingly, physicochemical properties of the co-existing layers as well as each of the materials should be examined in detail concerning with fuel recycling, inventory and so on.

We investigated changes in the surface states of two types of Be and C co-existing samples by means of x-ray photoelectron spectroscopy (XPS) along with secondary ion mass spectroscopy (SIMS). Trapping of deuterium was also investigated before and after sample preparation. The properties of the co-existing layers will be discussed on the basis of chemical bonding states of Be and C, and affinity to hydrogen.

2. Experimental

2.1. Sample preparation

Two types of co-existing samples of Be and C were prepared. One is the Be plate covered with evaporated carbon film (denoted as [C/Be]), and the other is the Be plate implanted with C₂H₄ ions, being simulated energetic carbon ion incidence, using a conventional ion gun (denoted as [C-Be]). Beryllium used was reactor grade hot-pressed plates purchased from NGK insulators. Its density and size were 1.85g/cm³ and 10×10×0.5mm, respectively. The purity is guaranteed as above 99.8%, where BeO was the main impurity (0.46mol%). The

detailed specification of Be is described elsewhere⁸.

The sample of [C/Be] was prepared by deposition of evaporating carbon on the Be plate at room temperature. Carbon deposition was carried out with arc discharge between two graphite rods (4mm in diameter) attached to the stainless steel electrode partly made of brass with applied voltage and current of 70V and 40A, respectively. The thickness of the deposited carbon film was 10nm which was measured using a calibrated quartz oscillator. On the other hand, the [C-Be] sample was prepared by implantation of C₂H₄ ions into Be which had been cleaned by Ar ion sputtering beforehand. The acceleration voltage and ion current were 5 kV and 20 μ A/cm², respectively. Total ion dose was 2×10^{18} ions/cm². C₂H₄ gas of pure grade was purchased from Sumitomo Seika. It was used without further purification.

2.2. XPS and SIMS measurement

An UHV system equipped with XPS and SIMS optics was used to measure changes in the surface state of the samples with vacuum heatings. The system was evacuated with a sputter ion pump and a turbomolecular pump backed with an oil-sealed rotary pump. The residual pressure of the system was routinely below 7×10^{-8} Pa.

The sample was mounted on a Ta-heater plate attached to the sample holder made of stainless steel. It could be heated up to 900°C, and its temperature was measured using a Pt/Pt-Rh(13%) thermocouple spot-welded to the backside of the Ta-heater. The sample was heated at a given temperature for 10 min, and was cooled to room temperature to measure XPS spectra. For XPS measurements, MgK α radiation (1253.6eV) with 400W power was used as probe. Energy of photoelectrons was measured with use of a cylindrical mirror analyzer (PHI 12-255). The binding energy readout was calibrated by referring the Au4f_{7/2} peak position as 83.7eV.

A conventional ion gun (PHI 04-191) was used for SIMS measurements and deuterium ion implantation. The probe of SIMS measurements was argon ions. Argon and deuterium gases were purchased from Nippon Sanso Co. (guaranteed as 99.999%) and Showa Denko Co. (guaranteed as 98%), respectively. They were used without further purification. Negative and/or positive secondary ions were measured using a quadrupole mass spectrometer (Extranuclear Lab., 19 mm rod, 1.5 MHz).

3. Results

3.1. [C/Be] sample

Fig. 1 shows the temperature dependence of wide range XPS spectra for the [C/Be]

sample. This figure shows that oxygen could not be completely removed from the surface only by vacuum heating, and the Be1s peak appeared by high temperature heating above 600°C. The LMM Auger transition peaks of Zn were observed in the range from 230 to 430eV. In addition, the Zn3s, -3p, and -3d peaks were also observed at 140, 90, and 10eV, respectively. This is probably due to contamination from overheated electrode used for carbon evaporation. They were disappeared above 600°C. On the other hand, Ta 4f and -4d peaks were observed at around 230 and 25eV. This is due to the signal from Ta-heater used to heat and/or hold the sample.

Fig. 2 shows change in the surface atomic composition with vacuum heating. The fraction of surface carbon was kept about 0.5 from room temperature to 400°C. Then it increased to 0.7 at 500°C, and rapidly decreased to an almost constant value of 0.2 in the range from 600 to 800°C. On the other hand, Be was not observed below 500°C. It appeared at 600°C and kept its surface fraction around 0.6. The surface atomic com-

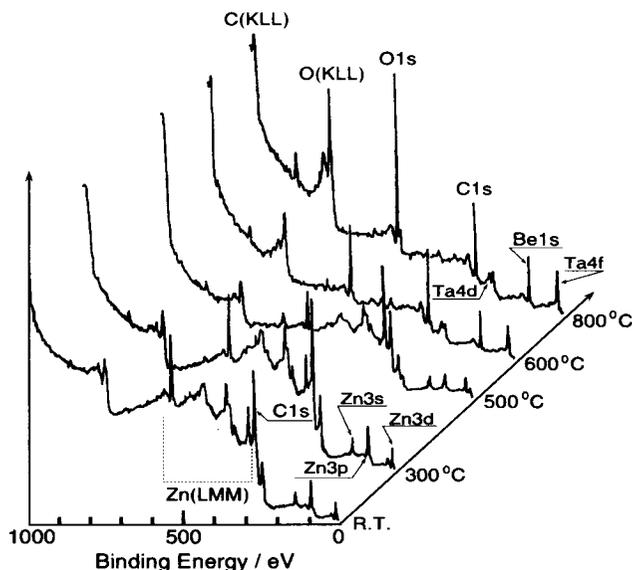


Fig.1 Change in the wide range XPS spectra of Be sampe covered with evaporated carbon film ([C-Be]) with vacuum heating.

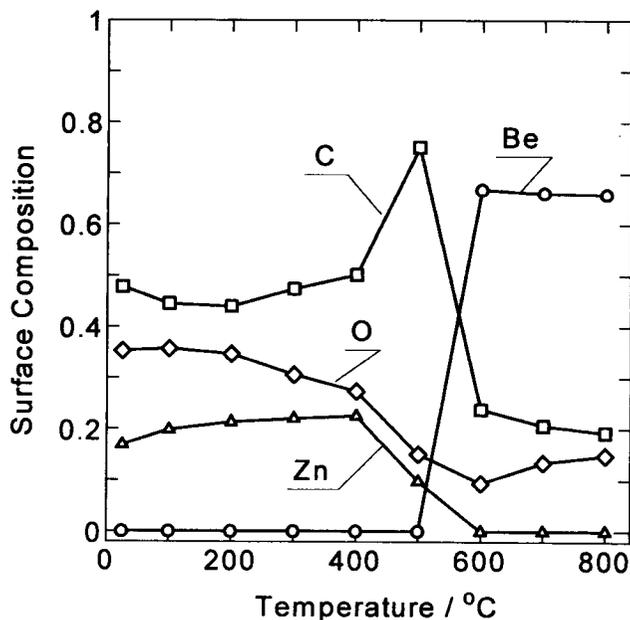


Fig.2 Change in the surface atomic composition of [C/Be] sample with vacuum heating.

position of oxygen was monotonously decreased from 0.4 to 0.1 with temperature rise to 600°C, and slightly increased above 600°C. The surface atomic fraction of Zn kept almost constant value of 0.2 from room temperature to 400°C, then it decreased to disappear above 600°C.

Fig. 3 shows temperature dependence of the Be1s XPS spectrum for the [C/Be] sample with vacuum heating. As seen in this figure, Be1s peak was not observed below 500°C, indicating that the Be surface was covered with deposited C layers. The Be1s peak appeared above 600°C at 112eV with a shoulder at higher binding energy side, indicating that surface Be atoms exist in two or more different chemical states on the sample surface.

Fig. 4 shows the temperature dependence of the C1s XPS spectrum for the [C/Be] sample with vacuum heating. A single C1s peak was observed irrespective to vacuum

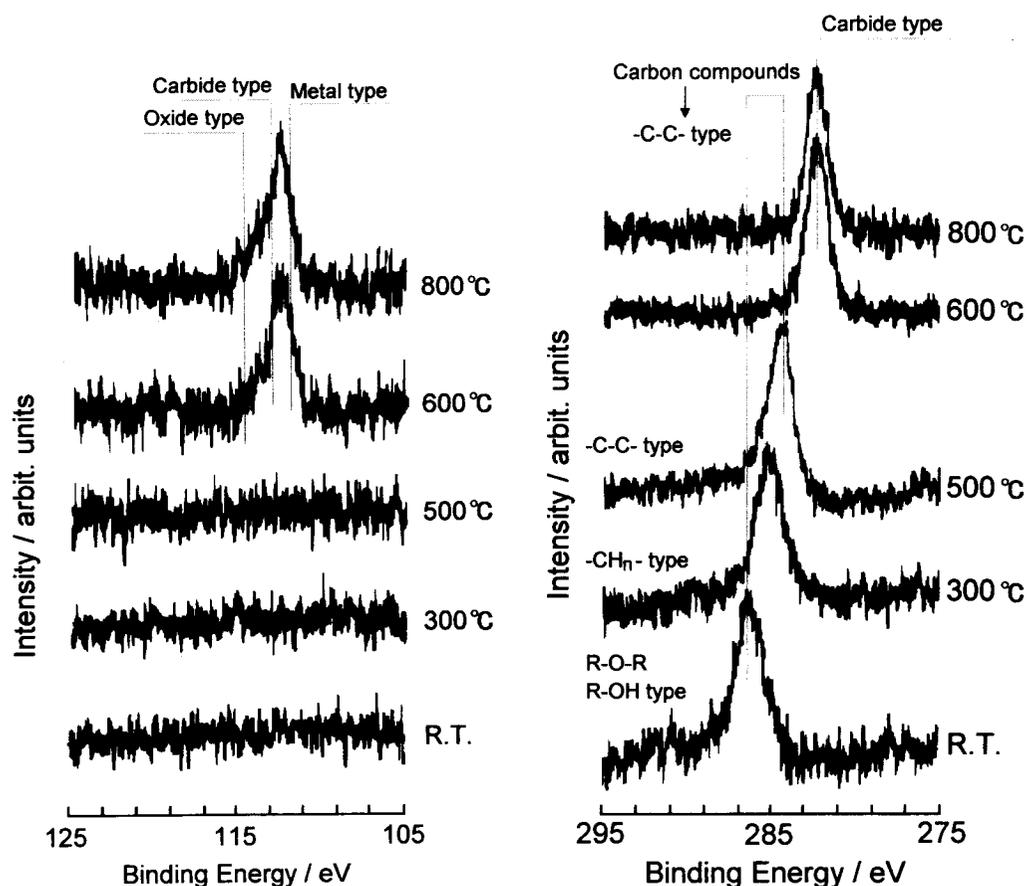


Fig. 3 Change in the narrow range Be1s spectra of [C/Be] sample with vacuum heating.

Fig. 4 Change in the narrow range C1s spectra of [C/Be] sample with vacuum heating.

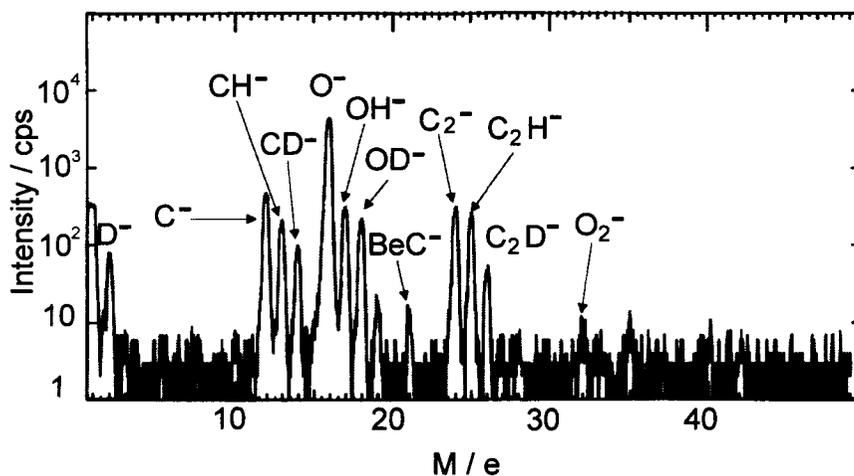


Fig. 5 Negative SIMS spectrum by argon in probe for [C/Be] at room temperature after deuterium ion implantation amounting to 1×10^{18} ions/cm². The sample was pre-annealed at 800°C for 10 min before deuterium implantation.

heating conditions. However, it shifted toward the lower binding energy side, in a range from 286 to 282eV, with increasing temperature to 600°C, and remained at 282 eV above 600°C.

Fig. 5 shows an example of negative SIMS spectra for [C/Be] sample which had been implanted with deuterium ions at room temperature after annealing at 800°C for 10 min. This spectrum was measured at room temperature using Ar⁺ ions as probe. Most of the peaks were attributed to the secondary ions relating to Be, C and oxygen (O); namely, $M/e = 12(C^-)$, $16(O^-)$, $21(BeC^-)$, $24(C_2^-)$, and $25(BeO^-)$. In addition, the species related to the implanted deuterium, such as $M/e = 2(D^-)$, $14(CD^-)$, $18(OD^-)$, $26(C_2D^-)$ and/or $BeOH^-$, and $27(BeOD^-)$ were observed. From this figure, it was found that deuterium atoms were captured by distinct trap sites: namely, O and C-sites.

3.2. [C-Be] sample

Fig. 6 shows the temperature

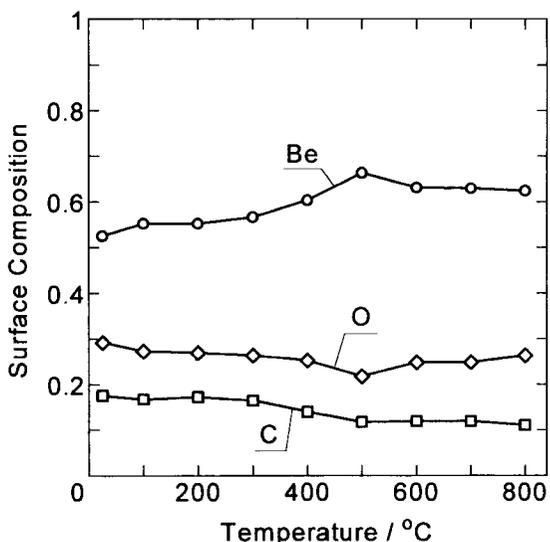


Fig. 6 Changes in the surface atomic composition for Be sample implanted with ethylene ions ([C-Be]) with vacuum heating.

dependence of surface atomic composition for the [C-Be] sample during vacuum heating. Be, C, and O were observed throughout a temperature range from room temperature to 800°C. From this figure, it was found that the surface atomic composition of Be slightly increased with increasing annealing temperature from room temperature to 500°C, then it kept almost constant value above this temperature. On the contrary, C gradually decreased with increasing temperature. O also gradually decreased below 500°C, and then slightly increased above this temperature. The surface atomic composition, however, did not change much by vacuum heating in comparison with that of [C/Be] sample.

Fig. 7 shows the temperature dependence of the Be1s XPS spectra of [C-Be] sample with vacuum heating. In the broad peaks observed at various heating temperatures, a feature of shoulders and/or double peaks were apparent. It indicates that Be atoms exist in two or more different chemical states on the surface.

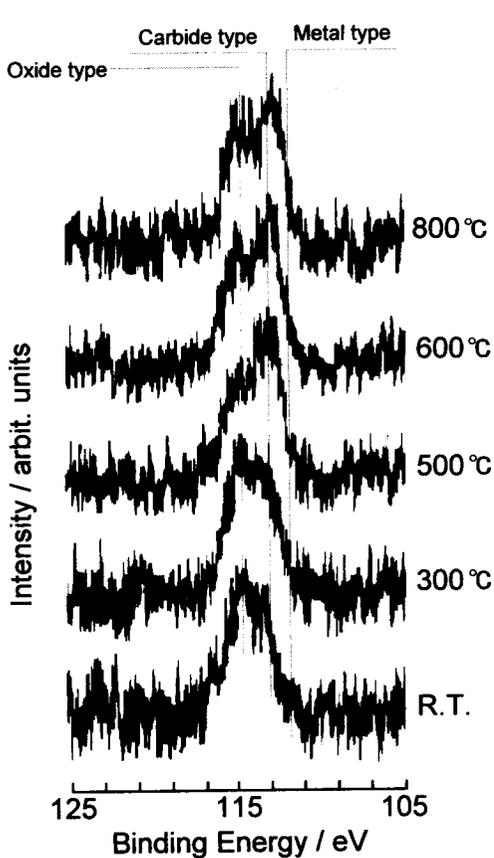


Fig. 7 Changes in the narrow range Be1s spectra of [C-Be] sample with vacuum heating.

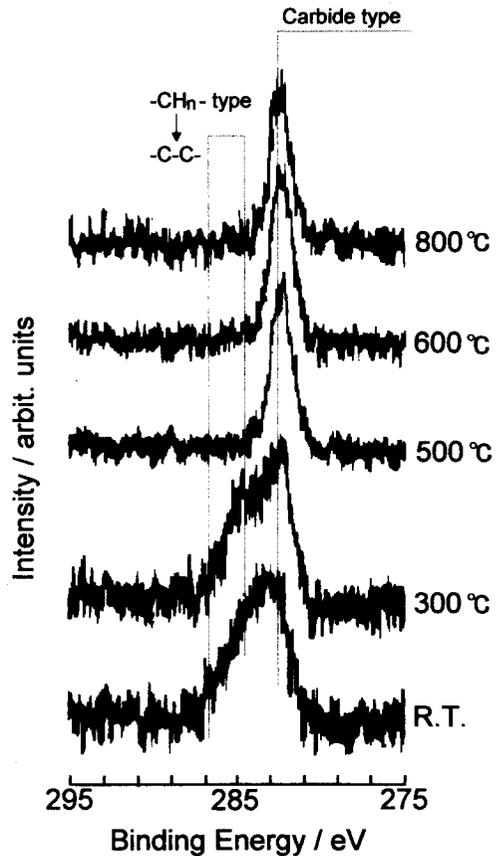


Fig. 8 Changes in the narrow range Cls spectra of [C-Be] sample with vacuum heating.

Fig. 8 shows the temperature dependence of the C1s XPS spectrum for [C-Be] sample with vacuum heating. From this figure, C1s peak was found to have a shoulder at higher binding energy side below 500°C. The results indicate that carbon atoms on the surface also exist in different chemical states. The C1s spectrum, however, changed to a single peak centered at 282eV above 500°C.

4. Discussion

4.1. Carbon deposited sample, [C/Be]

As shown in Fig. 4, the C1s peak shifted toward the lower binding energy side with increasing annealing temperature. According to the literature⁹⁻¹¹ the peak shift should be ascribed to the change in the chemical states of deposited carbon atoms. The binding energy of C1s peak of the as-prepared [C/Be] sample (286.5eV) was higher than that of graphite. It indicates that carbon layer contains impurities such as hydrogen, oxygen and/or hydroxide. They reduce the electron density of carbon atoms to increase the apparent binding energy of C1s electrons. These impurities might be included by the carbon layer during the deposition from residual gases due to the poor vacuum condition of the sample preparation chamber (1.3×10^{-4} Pa or higher). The C1s peak of 285eV observed after 300°C heating should be attributed to hydrogen containing carbon. The C1s peak of 284eV should be attributed to pure carbon. These observations suggest that most of the impurities included in the deposited carbon layers desorb to form volatile gases such as CO, CO₂, H₂O and hydrocarbons during the annealing. The final C1s peak of 283.5eV corresponds to metal carbides, indicating that the most part of carbon atoms changed to Be-carbide.

The observed Be1s peak could be deconvoluted into three component

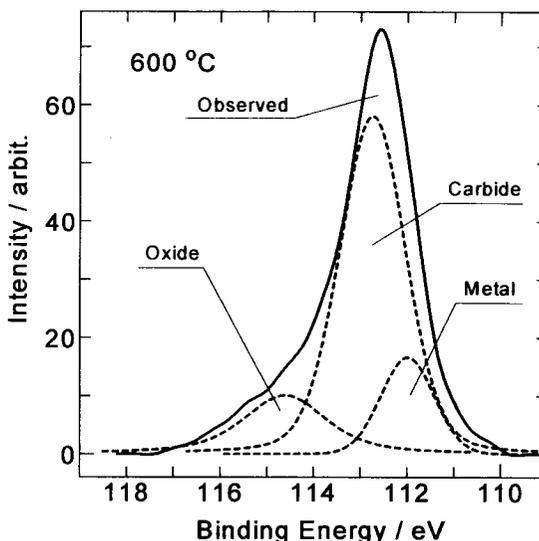


Fig. 9 Observed Be1s spectrum (solid line) of [C/Be] sample after heating at 600°C for 10 min could be deconvoluted into three component peaks (dotted lines). The peak at higher binding energy side could be assigned to Be-oxide, the middle to Be-carbide, and the lower to pure Be.

peaks by the least square spectral fitting calculations. Fig.9 shows the deconvolution of the Be1s spectrum for the [C/Be] sample heated at 600°C for 10 min. In this figure, the solid line shows the observed peak and dotted lines calculated component peaks. With respect to the component peaks, the most intense peak centered at 113eV could be ascribed to Be-carbide. One of the two weak peaks centered at 115eV could be ascribed to Be-oxide, and the other at 112eV to pure metallic state. The ratio of integrated peak intensities of these component peaks was [carbide] : [oxide] : [metal] = 5 : 1 : 1. On the other hand, from Fig. 2, surface atomic composition of Be, C and O after annealing at 600°C was 65%, 23% and 10%, respectively. Taking the results of deconvolution into account, atomic ratio of the surface Be-carbide is determined to be [Be] : [C] = 46% : 23% = 2 : 1. Therefore, the chemical formula of the Be-carbide should be written by Be₂C. Similarly, atomic ratio in the Be-oxide is determined to be [Be] : [O] = 9% : 10% ≈ 1 : 1, corresponding to the chemical formula of BeO, which is well known as commonly observed impurity on/in Be. Concerning the chemical states of Be above 600°C, most of the surface Be was found to exist as Be-carbide for [C/Be] sample. The formation of Be-carbide corresponds to the drastic change in the surface atomic composition above 600°C as shown in Fig. 4. This indicates that Be migrates fast to the surface from inner layers at higher temperature region above 600°C and reacts with surface carbon atoms as



4.2. Carbon implanted sample, [C-Be]

The observed C1s spectrum consisted of a peak centered at 283.5eV and shoulder at higher binding energy side, as shown in Fig. 8. This result indicates that carbon atoms exist both as carbide and amorphous hydrocarbons⁹⁻¹¹ below 500°C. Be and carbon atoms do not react easily to form Be₂C at around room temperature as shown in Figs. 3 and 4. The existence of Be₂C at room temperature suggests that local mixing and reaction of implanted carbon (ethylene ions) with surface Be atoms occurred due to the energy deposition/transfer caused by ion bombardment. In addition, the observed shoulder peak disappeared, and only a C1s peak centered at 283.5eV was observed above 500°C. It indicates that amorphous hydrocarbons on the sample surface decompose to form Be₂C according to the reaction (1).

The observed Be1s peaks showed more complicated spectra, as shown in Fig.7, suggesting that it consisted of two or more component peaks. They could be deconvoluted into three peaks by the least square spectral fitting calculations. Fig.10-(a)

and -(b) show examples of the deconvolution calculations for the [C-Be] sample heated at 300 and 600°C for 10 min, respectively. In this figure, solid line shows observed Be1s peak and dotted lines calculated component peaks. The ratio of integrated peak intensities of the component peaks was [carbide]:[oxide]:[metal]= 3 : 2 : 0 and 6 : 6 : 1 for the sample heated at 300 and 600°C, respectively.

From Fig. 6, surface atomic composition is [Be]:[O]:[C]=54%:28%:18% for the sample annealed at 300°C. Oxygen and a part of beryllium forms BeO as mentioned above. Excluding this oxide contribution, the ratio of oxygen free beryllium to carbon ratio should be [Be]:[C]=11:9. The deviation from Be₂C stoichiometry suggests the existence of excess carbon atoms on the sample surface. This consideration is in good agreement with that of the observed C1s spectra below 500°C that indicates the existence of amorphous hydrocarbons. Similarly, the ratio of [Be]:[O] is evaluated to be 32%:28%, almost equal to unity. Therefore the chemical formula of Be-oxide should be written by BeO. On the other hand, surface atomic composition is [Be]:[O]:[C]=61%:26%:13% for the sample annealed at 600°C. According to the results of deconvolution calculation, beryllium to carbon ratio is [Be]:[C]=28%:13% \div 2 : 1. Therefore, the chemical formula of Be-carbid should be written by Be₂C. Atomic ratio of Be-oxide is also concluded to be [Be]:[O]=28%:26% \div 1 : 1. The chemical formula of Be-oxide should be written by BeO.

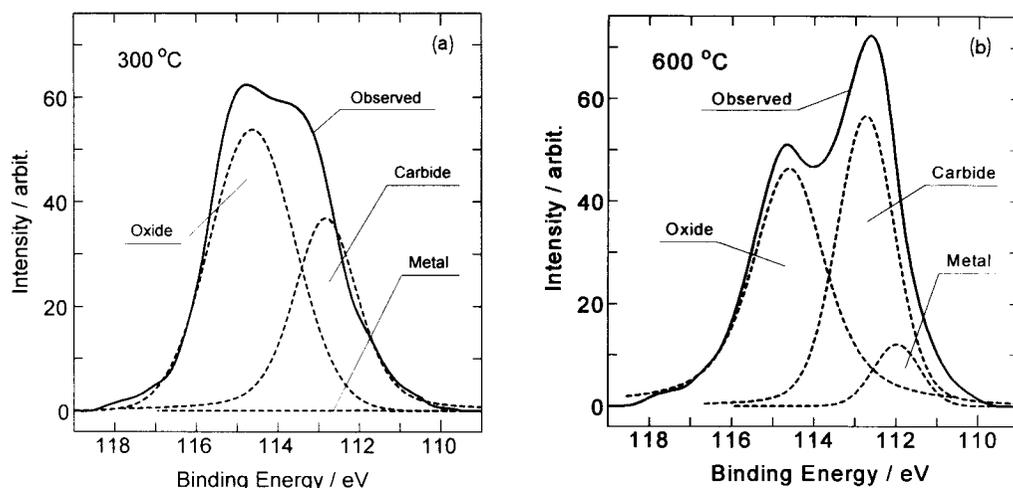


Fig.10 Observed Be1s spectra (solid line) of [C-Be] sample after heating at 300, (a), and/or 600°C, (b) for 10 min. These spectra could be deconvoluted into three component peaks (dotted lines). The peak at higher binding energy side could be assigned to Be-oxide, the middle to Be-carbide, and the lower to pure Be.

4.3. SIMS measurements

4.3.1 Carbon related species

Observed secondary ions of $M/e=12$ and 24 are typical species from carbon and/or graphite¹², and they should be assigned to C^- and C_2^- , respectively. Accordingly, peaks at 13 and 14 should be due to CH^- and CD^- , respectively. Although the latter (CD^-) seems also ascribed to CH_2^- , the above conclusion is supported by the absence of the CHD^- ($M/e=15$). Similarly, peaks at 25 and 26 were also assigned to C_2H^- and C_2D^- , respectively. Then, it is concluded that hydrogen isotope atoms are captured by carbon atoms on the sample surface.

XPS measurements revealed that Be_2C was formed both on the $[C/Be]$ and $[C-Be]$ samples. SIMS measurements also showed evidence of Be_2C formation : namely, negatively charged secondary ion of $M/e=21$ (BeC^-) was observed. On the other hand, hydrogen and/or deuterium atoms captured by BeC were not found in the present study. It indicates that the Be-carbide can not capture/ trap hydrogen isotope atoms.

4.3.2 Oxygen related species

The peak at $M/e=16$ should be assigned to O^- because the possibility of CD_2^- is eliminated by the absence of CHD^- . Peaks at 17 and 18 are assigned to OH^- and OD^- , respectively. From this observations, it is concluded that hydrogen isotope atoms were captured by oxygen atoms as $-OX$ ($X=H$ and D) on the sample surface. The peak at 19 is assigned to F^- captured in Be during its refining processes.

5 . Conclusions

In the present study, we have analyzed the changes in the chemical states of the two types of co-existing samples of Be and C with vacuum heating. One is the Be plate covered with evaporated carbon film, and the other is the Be plate implanted with C_2H_4 ions.

From the XPS measurements, it is concluded that the Be-oxide inevitably exists on the sample surface because of the strong affinity of Be to oxygen. It could not be completely removed from the surface only by vacuum heating. The stoichiometry of the Be-oxide is $Be:O=1:1$, corresponding to the chemical formula of BeO for both samples. It is also concluded that carbide formation takes place above $600^\circ C$. The chemical formula of the Be-carbide is written by Be_2C . In addition, the existence of Be_2C at around room temperature for the sample implanted with C_2H_4 ions indicates

that Be₂C would be formed at low temperatures due to the local energy transfer and/or deposition by energetic carbon ion incidence.

Based on the SIMS measurements, it is concluded that hydrogen isotope atoms are captured by carbon atoms on the sample surface. Carbon atoms, however, lose its ability to bind with hydrogen isotope atoms when it forms carbide. It would be a key to control hydrogen inventory in Be first wall. In addition, it is concluded that hydrogen isotope atoms were captured by oxygen atoms as -OX (X = H and D) on the sample surface. Previous SIMS investigations indicate that beryllium atoms have ability to capture hydrogen isotope atoms as Be-X⁸. Namely, hydrogen isotope atoms are concluded to be trapped on the sample surfaces by three distinct sites; Be, C, and O-sites.

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