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Release of hydrogen molecules from hydrogen-containing carbon film deposited on molybdenum

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Abstract

Molybdenum (Mo) plates covered with a hydrogen-containing carbon film, C(H)/Mo, were prepared as a model system to simulate carbon–metal mixed materials. The C(H)/Mo samples annealed at given temperatures and times in vacuum were analyzed by means of X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), thermal desorption spectroscopy (TDS) along with X-ray diffraction measurements (XRD). The XPS measurements revealed that the sample surface was covered with a carbon film containing hydrogen and a small amount of oxygen below 773 K. The $Mo3d_{5/2}$ peak appeared only after annealing at 873 K for 600 s, indicating that carbon atoms diffused to the bulk of Mo. The XRD measurements showed that Mo_2C formed in the surface layer after annealing at 1073 K for 600 s. In addition, it was observed with TDS that hydrogen molecules desorbed from the sample above 873 K. All of the above observations indicate that solid state chemical reactions take place at relatively low temperatures to cause Mo_2C formation and H_2 release in the subsurface layer or out of the C(H)/Mo system.

Keywords: Molybdenum; Carbon deposition; Material mixing

1. Introduction

Low-Z materials such as beryllium (Be), boron (B) and carbon (C) have improved plasma confinement parameters by the reduction of radiation loss for plasma energy [1,2]. However, their high erosion rate and/or low evaporation temperatures now become a serious concern when they are used as protective tiles on the inner wall of tokamaks. On the other hand, high-Z materials such as molybdenum (Mo) and tungsten (W) have advantages to compensate for low-Z materials with their durability against high heat loadings, low sputtering rate and so on [3].

In the next generation tokamak, two or more plasma facing materials (PFMs) will be installed together to control plasma surface interactions. The inner wall of such a machine will be sputtered by energetic fuel and impurity particles during operation, and then the sputtered particles are implanted and/or deposited on the wall to form a mixed material mainly consisting of constituents of the PFMs as well as fuel particles. Little is known, however, about the changes in the physico-chemical properties of mixed materials under various conditions. Therefore, knowledge of the nature of such mixed materials will be the key issue to control fuel recycling and inventory in the PFMs.

In the present study, a Mo plate covered with a hydrogen-containing carbon film, C(H)/Mo, was prepared as a model system to simulate carbon-metal mixed materials. Thermal desorption spectra (TDS) of gases from C(H)/Mo are discussed on the basis of surface chemical reactions caused by heat loading in vacuum along with the results obtained by surface characterization techniques of X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) and X-ray diffraction measurement (XRD).

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2. Experimental

2.1. Sample preparation

A molybdenum plate was used as base material. Its size was 10 × 10 × 0.5 mm. The purity was guaranteed to be over 99.999%, where the main impurities were tungsten (200 ppm), iron (50 ppm) and oxygen (20 ppm). Ethylene (C_2H_4) gas of pure grade was used as working gas for deposition of hydrogen-containing carbon film on the Mo substrate. It was purchased from Sumitomo Seika and used without further purification.

The samples used were prepared by use of a high vacuum system equipped with a quartz sample tube of 15 mm diameter, a quadrupole mass spectrometer (ULVAC MSQ-150A), a sputter-ion pump and a turbomolecular pump backed with an oil-sealed rotary pump. The residual pressure was routinely below 1×10^{-5} Pa. The quartz tube could be heated up to 1273 K, where the temperature was measured with a Pt/Pt–Rh (13%) thermocouple attached to the outside surface of the quartz tube. A Mo plate was put in the sample tube. It was annealed at 1273 K for 600 s in vacuum to desorb ad/absorbed gases, and cooled down to room temperature. Subsequently, C_2H_4 gas was introduced into the quartz tube at a pressure of 40 Pa and an rf discharge was started by outer loading coil to deposit hydrogen-containing carbon film on the Mo plate [4]. The frequency and the power applied for discharge were 13.56 MHz and 40 W, respectively. Hereafter, the Mo plate deposited with hydrogen-containing carbon film is denoted as C(H)/Mo in this paper.

2.2. XPS and SIMS measurements

The C(H)/Mo sample was taken out to the air to transfer to another ultra high vacuum system installed with SIMS and XPS. It was mounted on a rotatable stainless steel holder that can be positioned for both the optics. To minimize the effect of residual gas adsorption, the vacuum chamber was evacuated below 1×10^{-6} Pa prior to analysis.

A 400 W Mg Kα radiation X-ray source with the energy of 1253.6 eV was used for XPS measurements. The photoelectron energy was measured with a cylindrical mirror analyzer (PHI 12-255). The binding energy readout was calibrated using the $Au4f_{7/2}$ peak center to be 87.3 eV as Ref. [5].

To investigate the trapping of hydrogen isotopes, SIMS measurements were carried out before and after deuterium ion implantations for C(H)/Mo that was annealed at 1073 K for 600 s in vacuum. Argon ions accelerated to 5 keV were used as probe for both positive and negative SIMS measurements. Deuterium and Argon gases were purchased from Showa Denko (guaranteed as 98%) and Nippon Sanso (guaranteed as 99.999%), respectively. They were used without further purification. Both positive and negative secondary ions were analyzed using a quadrupole mass spectrometer (Extranuclear Lab., 19 mm rod with 1.5 MHz).

2.3. XRD and TDS measurements

XRD patterns were measured to examine the crystallographic change in the surface layer of C(H)/Mo before and after heating in vacuum. After surface characterization of an as-deposited C(H)/Mo sample at room temperature, it was put into a quartz tube attached to the vacuum system for heating under given conditions. Subsequently, the sample was cooled to room temperature, it was put into a quartz tube attached to the vacuum system for heating under given conditions. Subsequently, the sample was cooled to room temperature, and moved to the air for XRD measurements. XRD patterns were recorded on an X-ray diffractometer, Phillips PW1700. The probe was the Cu Kα line at 0.1572 nm operated 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 could be heated linearly with time from room temperature to 1073 K for TDS. The heating rate was 9 K/min. The partial pressures of desorbing gases were measured with a quadrupole mass spectrometer (ULVAC MSQ-150A).

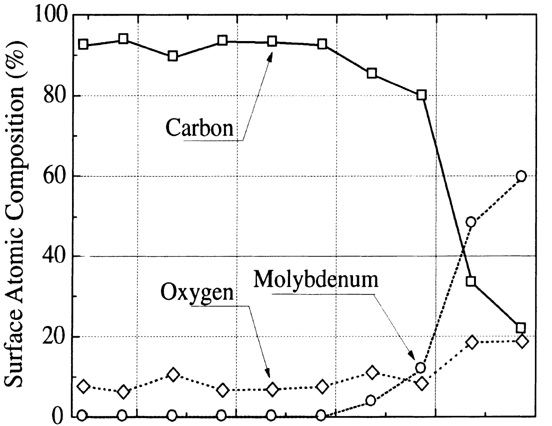

Fig. 1. Changes in the surface atomic composition of C(H)/Mo sample with annealing temperature measured with XPS.

3. Results and discussion

3.1. Changes in the surface states

From the ratios among integrated XPS peaks of C1s, O1s and Mo3d, the surface atomic composition was evaluated. Fig. 1 shows changes in the surface atomic composition of a C(H)/Mo sample with annealing temperature. Each of the measurements was carried out at room temperature after annealing at a given temperature for 600 s. No molybdenum was observed below 800 K, indicating that the sample surface was covered with deposited hydrogen-containing carbon film. Mo appeared above 873 K and its intensity gradually increased to reach 55 at.% at 1173 K. On the other hand, the carbon signal kept at almost a constant value around 90 at.% below 773 K, and then decreased to 21 at.% at 1173 K. In addition, the O1s remained almost constant around 10 at.% below 973 K and increased slightly to reach 19 at.% above 1073 K.

Fig. 2 shows changes in the binding energies of O1s, C1s and Mo3d$_{5/2}$ with annealing temperature. Below 673 K, the C1s peak was observed around 285.5 eV, indicating that the carbon film contains hydrogen in it. Above 673 K, the C1s peak gradually shifted toward the lower binding energy side to reach 282.5 eV which is lower than that of amorphous carbon and/or graphite, 284.5 eV. These observations suggest that the deposited carbonaceous film released hydrogen and changed to metal carbide [5–7]. The O1s peak was small, but could be deconvoluted to components peaked at 533 and 531 eV below 673 K, which correspond to –OH and –CO, respectively [7–9]. The former disappeared and the latter weakened above 673 K. However, a new peak appeared around 530 eV. The new peak is attributable to metal-oxide. This indicates that a part of adsorbed oxygen (–OH and –CO) changed to form metal-oxide. The changes in the chemical states of C and O were reflected in Mo3d$_{5/2}$ spectrum. Namely, its binding energy slightly increased from 227.7 eV to reach a constant value of 227.9 eV above 1073 K, indicating that Mo compounds were formed on the surface. Therefore, it is concluded that the deposited carbon film reacts with the Mo substrate to form a surface Mo-carbide layer, which contains a small amount of Mo-oxide.

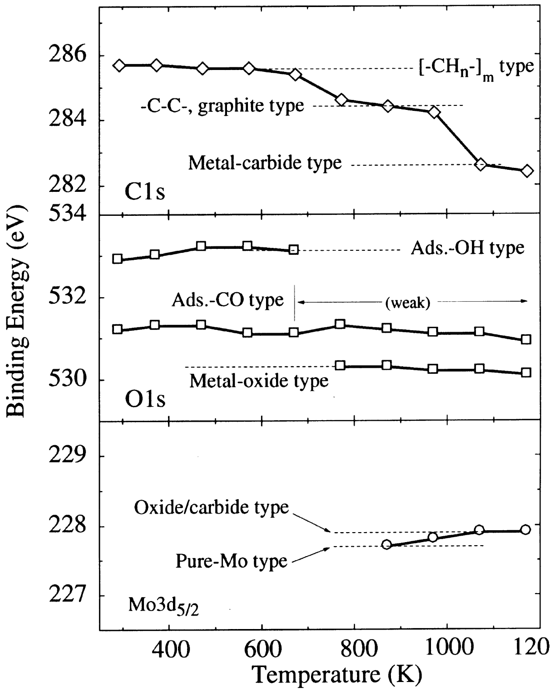

Fig. 2. Changes in the binding energies of O1s, C1s and Mo3d$_{5/2}$ with annealing temperature.

From Fig. 1, the surface atomic composition of Mo, C and O after annealing at 1173 K was determined to be 59, 22 and 19 at.%. This surface composition is equivalent to the atomic ratios of Mo : C = 2 : 1 and Mo : O = 1 : 1, suggesting that all Mo atoms on the surface reacted to form Mo-carbide or Mo-oxide.

Fig. 3 shows changes in the XRD patterns for the as-deposited C(H)/Mo (lower) and the annealed samples at 1073 K for 600 s (upper), respectively. The former shows no diffraction peak relating to the deposited carbon film. All of the observed peaks were due to metallic Mo. However, new diffraction peaks were observed after annealing at 1073 K for 600 s in vacuum. They could be assigned to Mo-carbide, Mo$_2$C. In addition, no other carbides such as MoC were observed. The appearance of

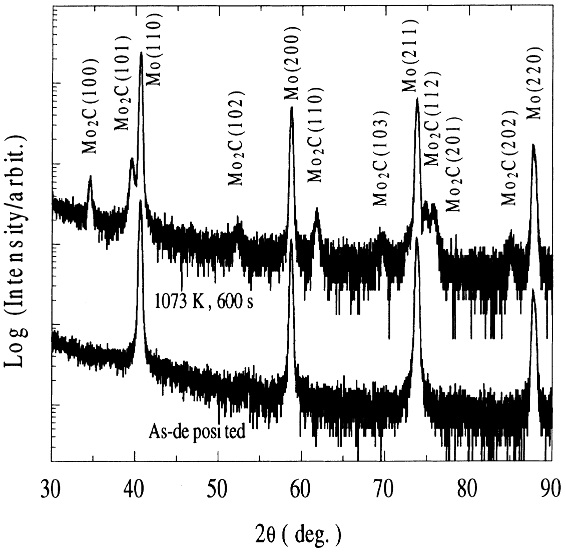

Fig. 3. Changes in the XRD patterns for the C(H)/Mo sample of as-deposited (lower) and annealed at 1073 K for 600 s (upper).

Mo_2C peaks is in good agreement with the XPS observations.

Fig. 4 shows the changes in the intensities of Mo_2C (1 0 0) and Mo_2C (1 1 0) peaks with isothermal annealing at 1073 K. They are normalized by the Mo (2 0 0) peak regarded as internal standard because this peak was intense enough and there was no other obstacle neighboring peaks around it. The isothermal annealing of the C(H)/Mo sample revealed that the intensities of Mo_2C peaks increased initially with annealing time till 3600 s, and then decreased in 9600 s. At the initial stage of the annealing, carbon atoms are expected to diffuse thermally into the interstitial sites of Mo lattice and eventually give rise to the growth of Mo_2C. On completion of Mo_2C formation, carbon migration from the surface carbide to the bulk should take place by further annealing, resulting in the reduction of the Mo_2C peaks. If these assumptions are valid, thickness of the Mo_2C layer could be simply estimated by $L = \sqrt{Dt}$. On account of diffusion data of C in Mo [9], the approximate maximum thickness of Mo_2C layer was about 4 mm, where the growth of Mo_2C layer was assumed to be completed at 3600 s.

3.2. Trap and release of hydrogen isotopes

Fig. 5 shows the TDS spectra of major desorption gases (H_2, CO and H_2O) from a C(H)/Mo sample (upper) and a bare Mo plate (lower). No appreciable release of hydrocarbons from the C(H)/Mo sample was observed in the present study. Both of the Mo plates were degassed at 1273 K for 600 s in vacuum to desorb adsorbed gases prior to use. For the Mo plate, the signal intensities were kept at almost background levels for $M/e = 2$ (H_2), 18 (H_2O) and 28 (CO) below 1100 K. However, the intensity of H_2 increased rapidly above 1100 K. This is mainly due to the desorption of H_2 from quartz tube [10]. On the other hand, the C(H)/Mo sample showed quite different TDSs, where H_2 and CO peaks appeared around 700 K and a H_2 peak around 950 K accompanied by a small CO peak.

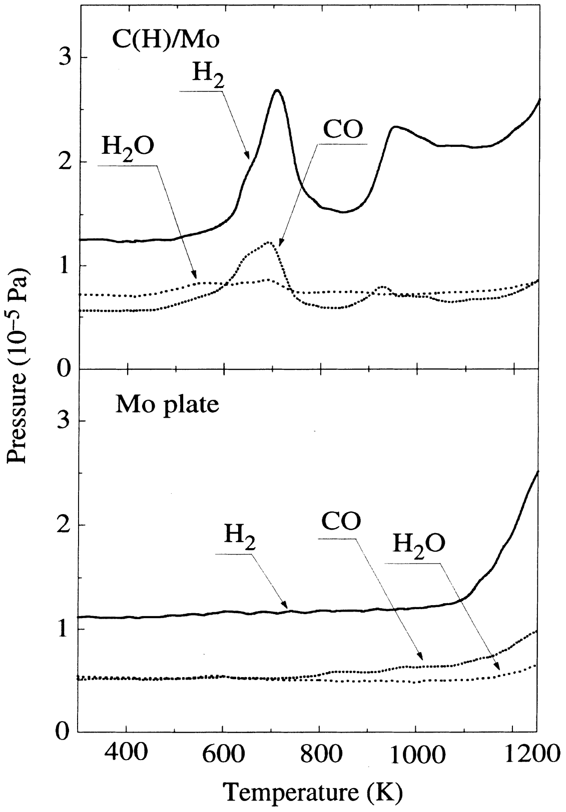

Fig. 5. TDS spectra of major desorption gases from bare Mo plate (lower) and C(H)/Mo sample (upper).

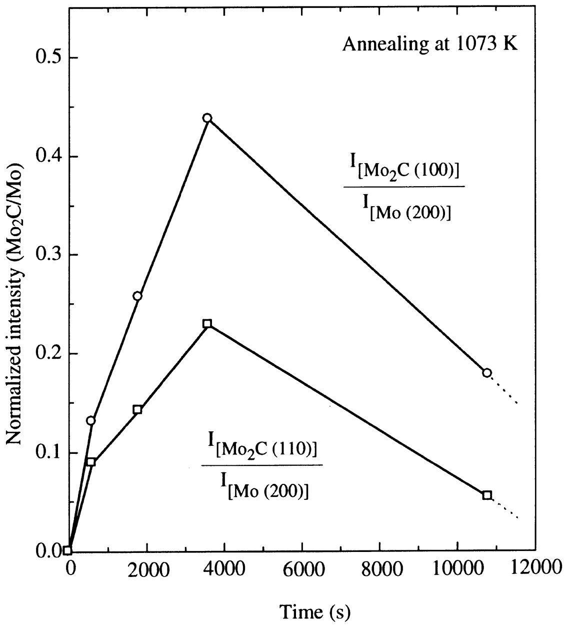

Fig. 4. Changes in the normalized intensities of Mo2C (1 0 0) and Mo (1 1 0) peaks with isothermal annealing at 1073 K.

On account of the XPS observations that no noticeable reaction takes place between the deposited carbon film and the substrate, the desorption peaks at the lower temperature side should be solely due to the carbon film. Because C–H has sufficient bond energy to keep it stabile against annealing [9], no desorption of H_2 can be expected only by vacuum annealing. On the other hand, adsorbed oxygen of –OH and –CO types observed in the low temperature region below 800 K (Fig. 2) strongly suggest the presence of adsorbed H_2O and CO on the C(H)/Mo surface. Therefore, reactions with adsorbed water molecules are highly plausible to take place [11]:

$$[\text{-CH}_n\text{-}]_m + x\text{H}_2\text{O(a)} \rightarrow x\text{C(O)} + (x + m'n'/2)\text{H}_2, \quad (n = 0\text{–}3, n > n', m > m'), \tag{1}$$

$$\text{C(O)} \rightarrow \text{CO(gas)}, \tag{2}$$

where $[\text{-CH}_n\text{-}]_m$ represents the hydrogen-containing carbon film deposited from C_2H_4 plasma on Mo plate, $H_2O(a)$ a water molecule adsorbed on the C(H)/Mo surface, and C(O) a carbon site occupied by adsorbed oxygen. The adsorbed water molecule is due to the air exposure during its transfer from the deposition device to the desorption measuring system. Therefore, the TDS peaks of H_2 and CO are concluded to be released by reaction Eqs. (1) and (2).

On the contrary, the second H_2 and CO peaks arise at the high temperature region above 850 K, where the reaction between the carbon film and the substrate becomes significant. This indicates that the desorption peaks of H_2 and CO at 950 K are obviously related with the formation of Mo_2C. Therefore, at the higher temperature region, desorption of gases could be expressed as follows.

$$[\text{-CH}_n\text{-}]_m + y\text{Mo} \rightarrow (y/2)\text{Mo}_2\text{C} + (m'n'/2)\text{H(a)}, \quad (n = 0\text{–}3, n > n', m > m'), \tag{3}$$

$$\text{Mo-oxide} + [\text{-CH}_n\text{-}]_m \rightarrow \text{Mo} + \text{CO(gas)} + (m'n')\text{H(a)}, \tag{4}$$

$$(m'n')\text{H(a)} \rightarrow \alpha\text{H}_2 + \beta\text{H(s)}, \quad (2\alpha + \beta = m'n'), \tag{5}$$

where H(a) is a hydrogen atom adsorbed on the surface, H(s) the hydrogen atom dissolved in the Mo substrate. The desorption amount of H_2 for C(H)/Mo, however, was rather small in comparison with C(H)/Be, which released a large amount of H_2 on formation of Be_2C above 800 K [11]. In addition, the temperature of Mo_2C formation is about 200 K higher than that of Be_2C for C(H)/Be [11]. The major difference between Mo and Be lies in the fact that the solubility of hydrogen in Mo is over one order of magnitude larger than that in Be [12,13]. It is highly plausible that $\alpha<\beta$ is valid for reaction (5) in this case: namely, a part of hydrogen desorbed from C(H)/Mo is likely to be dissolved in the bulk of Mo substrate.

Fig. 6 shows examples of negative SIMS spectra of the annealed sample before (lower) and after (upper) deuterium ion implantation. The SIMS spectra were recorded in a range from $M/e = 1$ to 45 to observe ion species relating hydrogen, deuterium, carbon and oxygen. Concerning the annealed sample, the observed secondary ion peaks were attributed to the species relating to oxygen and carbon: namely, $M/e = 16$ (O^-), 17 (OH^-), 32 (O_2^-), and 12 (C^-), 13 (CH^-), 24 (C_2^-), 25 (C_2H^-) and 26 ($C_2H_2^-$). The most intense peak at $M/e = 16$ suggests the presence of Mo-oxide on the sample surface because most of the oxygen bound and/or adsorbed to carbon desorbed as CO. Other peaks should be assigned to $M/e = 19$ to F^-, 35 and 37 to $^{35}Cl^-$ and $^{37}Cl^-$. They were considered due to impurity elements mixed in manufacturing process of Mo.

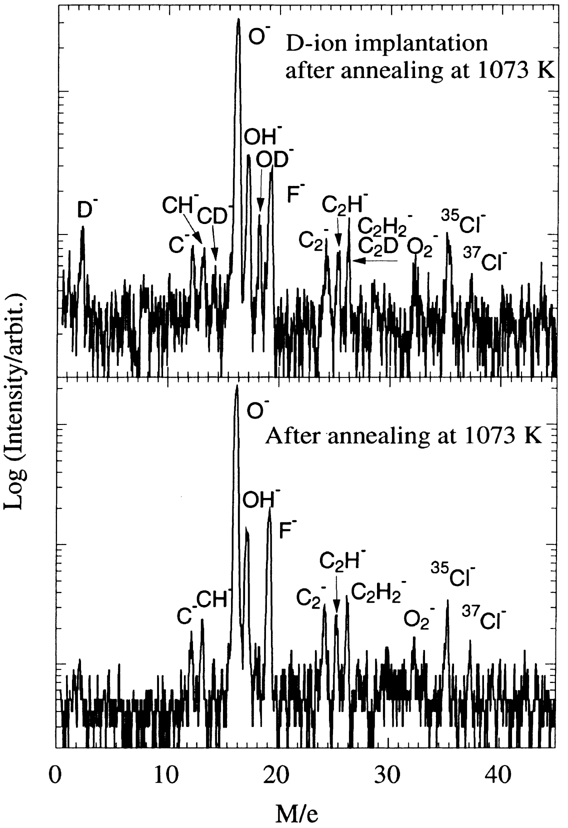

Fig. 6. Negative SIMS spectra of the annealed sample before (lower) and after (upper) deuterium ion implantation.

New peaks were observed after deuterium ion implantation. They were attributed to the secondary ions relating to deuterium: namely, $M/e = 2$ (D^-), 14 (CD^-), 18 (OD^-) and 26 (C_2D^-). Peaks of deuterium atoms bound to carbon, however, showed very small intensities in comparison with those observed for graphite implanted with deuterium ions [14]. In addition, peak at $M/e = 2$ (D^-) indicates the presence of deuterium atoms, presumably trapped in Mo_2C and/or Mo matrix on the surface. It is concluded, therefore, that carbon atoms lose their ability to bind with hydrogen isotope atoms on forming carbide, Mo_2C.

It is worthwhile to mention here that the chemical reactivity of hydrogen containing carbon films is expected to differ from each other depending on their chemical composition, average molecular weight, structure and so on [15]. Therefore, it is of great importance to study fundamental properties of well-characterized carbon films to understand physicochemical characteristics of those formed in tokamaks.

4. Conclusions

The model of mixed materials consisting of hydrogen, carbon and molybdenum, C(H)/Mo, revealed that thermochemical reactions take place between hydrogen-containing carbon layer, which will grow on the first wall of a nuclear fusion device, and high-Z wall material as well as oxygen-containing gases or adsorbed species. The conclusions of this study are summarized as follows:

1. Formation of Mo_2C takes place with vacuum annealing at 1073 K for 600 s. This temperature is about 200 K higher than that observed for C(H)/Be system [11].
2. Hydrogen is released from C(H)/Mo system through the reaction between carbon and molybdenum. This is because carbon atoms lose their ability to capture hydrogen by carbide formation. The loss of hydrogen affinity is one of the key issues to control fusion fuel balance as far as hydrogen-containing carbon and high-Z materials like Mo are concerned.
3. A part of hydrogen desorbed from C(H)/Mo at a high temperature region is likely to be dissolved in the bulk of Mo substrate. The distribution of evolved hydrogen between gas and solid phases should differ much from system to system. This is also a serious concern to control fuel inventory in the mixed materials formed on the first wall of tokamaks.

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