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Citation	北海道大學工學部研究報告, 169, 41-48
Issue Date	1994-06-28
Doc URL	https://hdl.handle.net/2115/42427
Type	departmental bulletin paper
File Information	169_41-48.pdf



Model for Hydrogen Retention and Chemical Sputtering of Boron-Carbon Plasma Facing Material

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(Received December 21, 1993)

Abstract

The model for hydrogen retention of boron carbide material used as the plasma facing wall in fusion devices is described. In this model, the hydrogen detrappings of C-H and B-H bondings are assumed as the rate determining step of the desorption. The hydrogen retention is observed to more rapidly decrease with the temperature, compared with a case of graphite. This tendency is similar to the experimental observation. Several parameters of thermal desorption and ion impact desorption are discussed based on the model.

For the chemical sputtering, the model is suggested to explain the yield and the peak temperature of boron carbide material. The comparison between the model and the experimental shows that the reduction of the yield in the boron carbide is due to one order of magnitude smaller reactivity of methane formation, compared with that of graphite.

1. Introduction

It is well known that the hydrogen recycling, defined by repeated motion of neutral hydrogen between the boundary plasma and the plasma facing wall in fusion devices such as tokamak, largely reduces the energy confinement time of plasma¹⁾. In the present large devices such as JET^{2),3)}, TFTR¹⁾ or JT-60U^{4),5)}, the inner wall of vacuum vessel has been entirely covered by graphite material. In a such case, the degree of the hydrogen recycling becomes large since the graphite extremely absorbs the fuel hydrogens due to the porous structure^{6),7),8)}. For the reduction of trapped or retained hydrogens, the techniques such as baking and He discharge cleanings have been often applied before the main plasma discharge shot, and the hydrogen recycling has been considerably suppressed now. By the success of the reduction of trapped hydrogens, the high energy confinement discharges called as H mode and Hot Ion Temperature Mode were obtained in the large tokamaks^{1),2)}.

It is also pointed out that there is the other problem associated with the graphite wall, e. g. the erosion in form of CO due to oxygen impurities of plasma, while the graphite showed excellent thermal stability to the high heat flux bombardment. Since the erosion yield is approximately unity, the carbon impurity level continuously increases by the oxygen recycling. In order to reduce the oxygen impurity level, the gettering material for oxygen such as B or Be has been now employed in form of coatings or carbide on the graphite wall^{1),2),3),4),5)}.

The oxygen impurity level was significantly reduced by using Be coatings, or coatings of B or boron carbide (B_4C). In addition, the chemical sputtering of the graphite in form of CH_4 due to hydrogen ions⁹⁾, was observed to be largely reduced by the use of boron.

In a case that the coatings of B or boron carbide is applied, however, the effect on the hydrogen recycling has not been clarified yet. Namely, the hydrogen retention properties of such material has not been examined systematically. In this note, the model for hydrogen retention of B_4C coated graphite is constructed, based on the model for the graphite⁹⁾. For the chemical sputtering of B_4C coated graphite¹⁰⁾, the model is presented. The discussions on the models are progressed by referring the experimental results recently obtained in our laboratory¹¹⁾.

2. Model for Hydrogen Retention

The model for the hydrogen retention of graphite is reviewed, and then the model for B_4C coated graphite is presented.

2.1 Hydrogen Retention of Graphite

Considered is the case that the graphite wall is exposed to hydrogen ions as shown in Fig. 1. The hydrogen ion may be trapped in the region from the surface to the depth at the projected range. During the irradiation, the detrapping also occurs due to thermal desorption and ion impact desorption. The hydrogen may be re-emitted in form of hydrogen molecule, after that the detrapped hydrogen atoms recombine each other in the surface. It is not clear that the rate determining step is the detrapping process or the recombination process. If the re-trapping rate of detrapped hydrogens is less than the recombination rate, it can be conceived that the detrapping process is the rate determining step. We here consider the model assuming the detrapping process being the rate determining step.

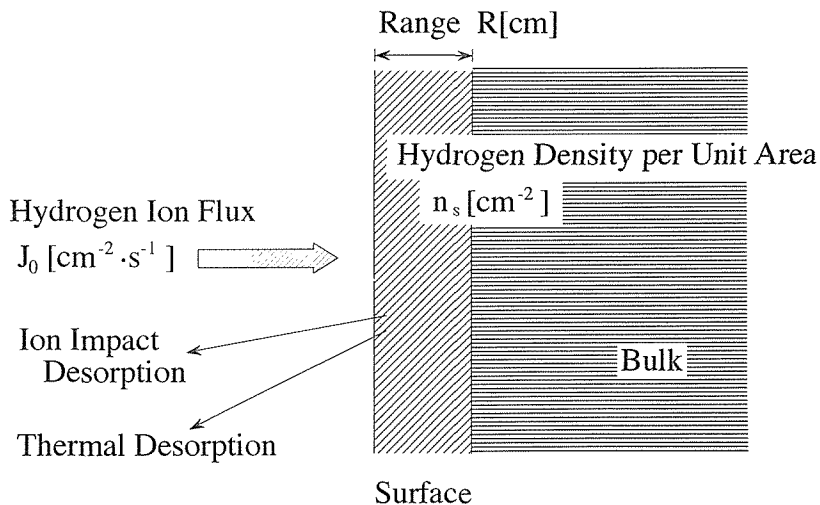


Fig. 1 Trapping and detrapping of hydrogen in graphite.

In order to evaluate the chemical sputtering, Erents⁹⁾ assumed the following density balance for trapped hydrogens

$$\frac{dn_s}{dt} = J_o - \nu n_s - \sigma J_o n_s, \quad (1)$$

where $\nu = \nu_o \exp(-E/kT)$ is the thermal desorption rate(/s), ν_o the frequency factor(/s), E the activation energy of thermal desorption(eV), k the Boltzmann constant (8.62×10^{-5} eV/K), T the temperature(K), J_o the hydrogen ion flux(/cm² · s), σ the cross section of ion impact desorption(cm²), and n_s the density of trapped hydrogen(/cm²). In a steady state, the density of trapped hydrogen becomes

$$n_s = \frac{1}{\sigma} \cdot \frac{1}{1 + \left(\frac{\nu_o}{\sigma J_o}\right) e^{-E/kT}}. \quad (2)$$

We now consider the temperature dependence of hydrogen retention. For the graphite, the maximum trapping is observed when the atomic ratio, H/C=0.4 at RT^0 . So the value of n_s in Eq.(2) can be estimated from the relation

$$\frac{n_s(T=RT)}{n_c R} = 0.4, \quad (3)$$

where R is the range of injected ion(cm), and n_c the carbon density of the graphite. In a case that the energy of ion is 1.5 keV, R is about 300 Å. Since $n_c = 8 \times 10^{22}$ /cm³, σ becomes 10^{-17} cm².

The peak temperature of the desorption can be obtained by the differentiations of Eq.(2) with respect to temperature, T . The peak temperature, T_p , is given by

$$\frac{1}{T_p} = -\frac{k}{E} \ln\left(\frac{\sigma J_o}{\nu_o}\right) \quad (4)$$

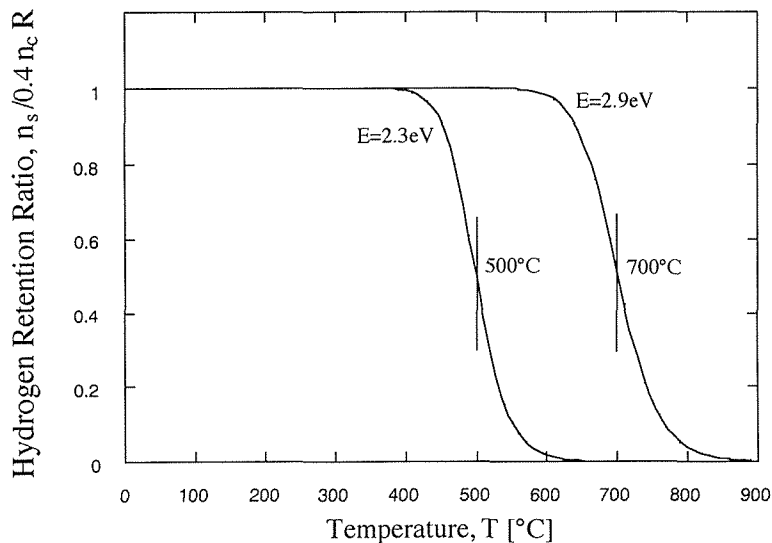


Fig. 2 Hydrogen retention ratio versus temperature for graphite.

In the thermal desorption experiment, the desorption peak is observed in the range from 500°C to 700°C. The range of the corresponding activation energy becomes from 2.3 eV to 2.9 eV when $J_0 = 10^{15}/\text{cm}^2 \cdot \text{s}$ and $\nu_0 = 10^{13}/\text{s}$. This estimation well corresponds to the experimental data obtained so far, e.g. 2-4 eV¹²⁾.

Figure 2 shows the hydrogen retention ratio versus temperature for cases with $E = 2.3$ eV and 2.9 eV. The hydrogen retention is normalized to the value at RT. The retention very rapidly decreases around at the peak temperature of desorption. The profile of hydrogen retention obtained in the experiment⁸⁾ has smoother distribution, compared with that of Fig. 2. Possible reason of the difference may be the broadening of the activation energy in the actual case.

2.2 Hydrogen Retention of Boron Carbide Coated Graphite

The B_4C coated graphite has been now used as the divertor wall in JT-60U¹⁰⁾. For this material, the thermal desorption experiments were carried out after the hydrogen ion irradiation¹¹⁾. Two major desorption peaks were observed in the spectrum at 350°C and 700°C. The high temperature peak is due to the detrapping of C-H bondings since the peak temperature is the same as that of graphite. For the boron film produced by plasma CVD, the hydrogen desorption peak was observed in the vicinity of 350°C in our experiment¹³⁾. This desorption occurs by the detrapping of B-H bondings. Therefore, the low temperature peak observed for the B_4C coated graphite is presumed to be due to the detrapping of B-H bondings.

In the B_4C coated graphite, the boron may exist in form of carbide, $\text{B}_4\text{C}^{14)}$. Since the atomic ratio, $\text{B}/\text{C} = 2$, the graphite also exists in the coating layer. When this material is exposed to hydrogen ions, the bondings of C-C, B-C and B-B will be destroyed multiply if the fluence is higher than about $10^{17}/\text{cm}^2$. Then, the injected ions should be trapped by C or B atom. From these arguments, it can be conceived that possible trapping states are C-H and B-H bondings.

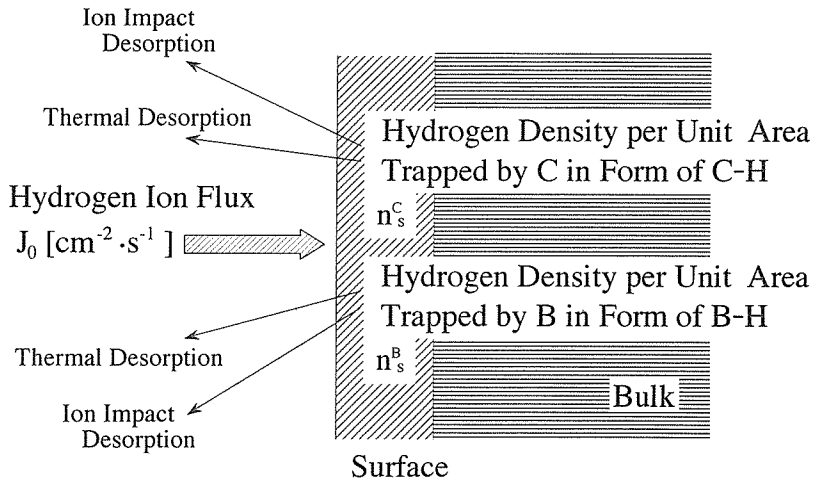


Fig. 3 Trapping and detrapping of hydrogen in B_4C coated graphite.

Figure 3 shows the hydrogen ion irradiation to the B₄C coated graphite. The balance equations for the densities for C-H and B-H trappings are written as

$$\frac{dn_s^C}{dt} = f_C J_0 - \nu_C n_s^C - \sigma n_s^C J_0, \quad (5)$$

$$\frac{dn_s^B}{dt} = f_B J_0 - \nu_B n_s^B - \sigma n_s^B J_0, \quad (6)$$

where super script or suffix, C or B, indicates the carbon or the boron, respectively, $f_{C,B}$ the fraction trapped by C or B, and $\nu_C = \nu_0^C \exp(-E_C/kT)$ and $\nu_B = \nu_0^B \exp(-E_B/kT)$. In a steady state, the trapped densities are expressed as

$$n_s^C = \frac{f_C}{\sigma} \cdot \frac{1}{1 + \left(\frac{\nu_0^C}{\sigma J_0}\right) e^{-E_C/RT}}, \quad (7)$$

$$n_s^B = \frac{f_B}{\sigma} \cdot \frac{1}{1 + \left(\frac{\nu_0^B}{\sigma J_0}\right) e^{-E_B/RT}}. \quad (8)$$

The peak temperatures of desorptions due to the detrappings of C-C and B-H bondings are given by

$$\frac{1}{T_F^C} = -\frac{k}{E_C} \ln\left(\frac{\sigma J_0}{\nu_0^C}\right), \quad (9)$$

$$\frac{1}{T_F^B} = -\frac{k}{E_B} \ln\left(\frac{\sigma J_0}{\nu_0^B}\right) \quad (10)$$

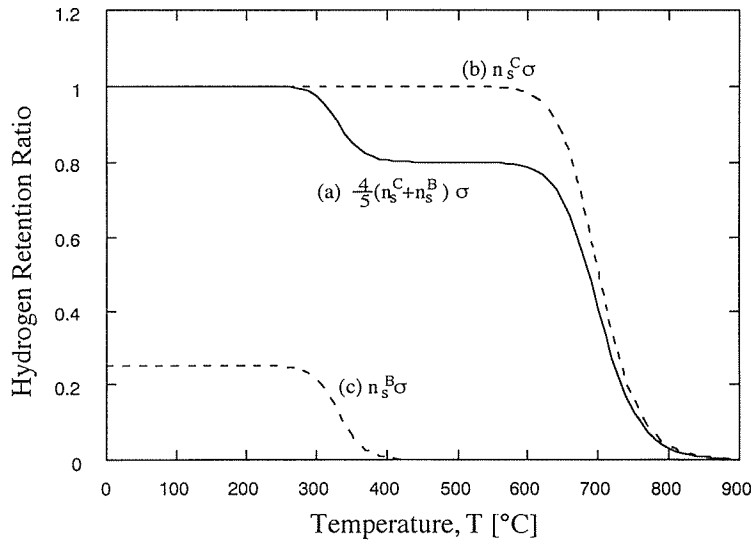


Fig. 4 Hydrogen retention ratio versus temperature for B₄C coated graphite.

- (a) Total retention ratio
- (b) Retention ratio of graphite component
- (c) Retention ratio of boron component

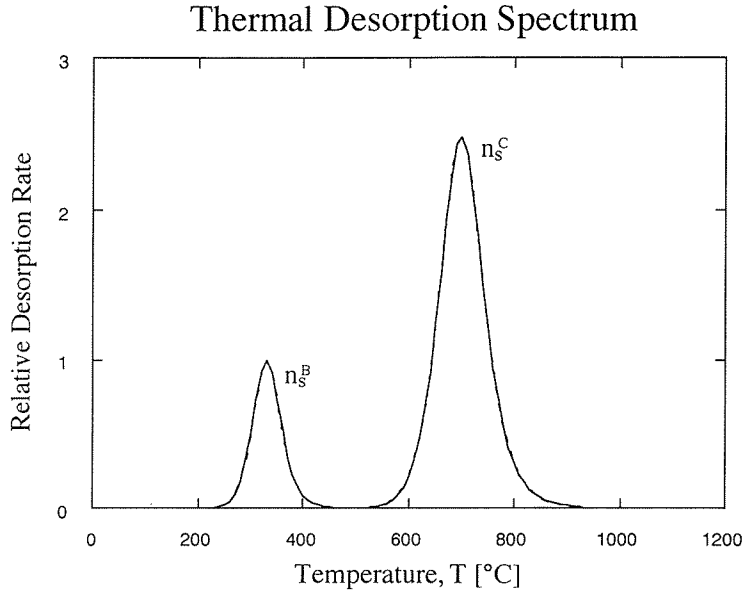


Fig. 5 Illustration of thermal desorption spectrum of B₄C coated graphite.

The experimental results showed that $f_B/f_C = 1/4^{11)}$. Thus, the trapping probability of C is 8 times larger than that of B, since $B/C=2$. It was also observed that $T^C_p = 700^\circ\text{C}$ and $T^B = 350^\circ\text{C}$. From Eqs.(9) and (10), then, the activation energies, E_C and E_B , becomes 2.9 eV and 1.8 eV, respectively, when $\sigma = 10^{-17}\text{cm}^2$, $\nu_0^C = \nu_0^B = 10^{13}/\text{s}$ and $J_0 = 10^{15}/\text{cm}^2 \cdot \text{s}$. Figure 4 shows the temperature dependence of hydrogen retention (Curve (a)), where the value at RT is normalized as unity. Compared with the case of graphite (Curve (b)), the decrease of the retention occurs at the temperature lower than that of the graphite. This tendency roughly agrees with the experimental observation¹¹⁾.

It is noted that the differentiations of Eqs.(7) and (8) give us the thermal desorption spectrum, which is illustrated in Fig. 5.

3. Model for Chemical Sputtering

We here consider the models for chemical sputterings of graphite and B₄C coated graphite.

3.1 Chemical Sputtering of Graphite

The chemical sputtering yield is expressed by the product of methane formation rate with the trapped hydrogen density⁹⁾

$$Y = \frac{Ae^{-E^*/kT} \cdot n_s}{J_0}, \quad (11)$$

where A is the coefficient of reactivity of CH₄ formation ($6 \times 10^7/\text{s}$), E^* the activation energy of CH₄ formation, Y the yield. The peak temperature of CH₄ desorption becomes

$$\frac{1}{T_P^*} = -\frac{k}{E} \ln\left(\frac{E^*}{E-E^*} \cdot \frac{\sigma J_o}{\nu_o}\right) \quad (12)$$

In the case that $E=2.4$ eV and $E^*=1.65$ eV, the peak temperature and the maximum yield are calculated as 600°C and 0.15, respectively. These results well agree with the experimental values obtained so far.

3.2 Chemical Sputtering of B₄C Coated Graphite

In this case, the hydrogens trapped by both C and B contribute to the formation of CH₄. Thus, the yield, Y_g , is given by

$$Y_g = A_g e^{-E_g^*/kT} \frac{n_S^C + n_S^B}{J_o}, \quad (13)$$

where A_g and E_g^* are the coefficient of reactivity and the activation energy of CH₄ formation in the case of B₄C coated graphite, respectively. The peak temperature of CH₄ desorption, e.g. the temperature corresponding to the maximum yields, becomes

$$\frac{1}{T_{P,C}^*} = -\frac{k}{E_C} \ln\left(\frac{E_g^*}{E_C-E_g^*} \cdot \frac{\sigma J_o}{\nu_o^C}\right), \quad (14)$$

$$\frac{1}{T_{P,B}^*} = -\frac{k}{E_B} \ln\left(\frac{E_g^*}{E_B-E_g^*} \cdot \frac{\sigma J_o}{\nu_o^B}\right) \quad (15)$$

The peak temperatures observed in the experiment¹¹⁾ were 600°C and 350°C. The yield was about one order of magnitude smaller than the of the graphite, the maximum of $Y_g=0.01$. If in Eqs.(14) and (15), $\nu_o^C=\nu_o^B=10^{13}/s$, $E_g^*=1.65$ eV, $E_C=2.4$ eV, $E_B=1.8$ eV, $\sigma=10^{-17}$ cm² and $J_o=10^{15}/\text{cm}^2 \cdot s$ are substituted, we have $T_{P,C}^*=550^\circ\text{C}$ and $T_{P,B}^*=380^\circ\text{C}$, which are close to the experimental values. From these results, the assumption for these parameters may be verified.

By using these parameters, we can calculate the maximum yield. If the value of A_g is $4 \times 10^6/s$, the maximum yield becomes experimental value (=0.01). On the other hand, the maximum yield in the case of the graphite was 0.15 and the coefficient of the reactivity, A , was $6 \times 10^7/s$, as described earlier. The coefficient of the reactivity in the case of B₄C coated graphite is one order of magnitude smaller than that of graphite. It is not clarified so far that the reason for reduction of chemical sputtering due to the boron carbide is the decrease of hydrogen retention at high temperature range or the decrease of the reactivity. The present discussion indicates that the decrease of the reactivity largely contributes to the reduction of the yield.

4. Discussion and Summary

The model for hydrogen retention of B₄C coated graphite is suggested, and discussed with the experimental results. It can be conceived that the hydrogen is trapped in forms of C-H and B-H bondings. The trapping probability of C to H is about one order of magnitude larger than that of B. Since the hydrogen detrapping for B-H bonding occurs at 350°C in

addition to the detrapping of C-H bonding at 700°C, the hydrogen retention should begin to decrease at lower temperature, compared with the case of graphite. The activation energy for the detrapping of B-H bonding is estimated as 1.8 eV, which is considerably smaller than that of C-H bonding. The present model may be useful to determine the unknown parameters of thermal and ion impact desorptions with the help of experimental data.

For the chemical sputtering of B₄C coated graphite, the expression of the yield is obtained. It is found that the reduction of the yield is due to the large decrease of the reactivity.

In a case that the boron material such as the present B₄C coated graphite is used as the plasma facing material in a fusion device, the baking with the temperature of 350°C as the pretreatment may be effective for the reduction of the hydrogen retention in form of B-H bonding.

Acknowledgements

The authors thank Drs. T. Ando and M. Akiba, Japan Atomic Energy Research Institute for their valuable discussions. Part of this work was carried out as the Collaborative Study of National Institute of Fusion Science.

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