



Properties of thin boron coatings formed during deuterated-boronization in JT-60

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Abstract

Since 1992, the boronization using B₁₀H₁₄ (decaborane-based boronization) has been utilized in JT-60 once or twice a year. It is very effective in reducing both the impurities, like oxygen and carbon, in the plasma and in recycling fuel particles. However, we needed ~ 500 discharges to exchange hydrogen in the boron film for deuterium, after the boronization using only He for a dilution gas. Using a mixed-dilution gas of He and deuterium, we made the boronized film on JT-60 first wall (deuterated-boronization). A typical composition of working gas was 2% B₁₀H₁₄, 38% D₂ and 60% He, which was used in a flow through situation. The amounts of hydrogen and deuterium in the boronized film were evaluated to be ~ 5 and ~ 30 at%, respectively. In addition, the deuteration factor of D/(H + D) in the first plasma after the boronization increased from less than 0.2 to 0.8. Thus, we can drastically reduce the number of the conditioning discharges from ~ 500 to ~ 50 for the isotope-exchange before D plasma experiments.

Keywords: JT-60U; Desorption; Wall coating; Low Z wall material; Wall particle retention

1. Introduction

The in situ deposition of boron containing films on all plasma exposed surfaces of a tokamak (i.e. boronization) was first developed in 1988 for the TEXTOR tokamak [1]. This process has since been used in several other tokamaks, such as ASDEX [2], TCA [3], TFTR [4], DIII-D [5] and Tore Supra [6]. In JT-60, the boronization using B₁₀H₁₄ (decaborane-based boronization) has been utilized once or twice a year [7]. It is very effective in reducing both the impurities, like oxygen and carbon, in the plasma and in the recycling of fuel particles [8]. However, we had two problems to be resolved relating to the boronization: the homogenization of the film deposition around the torus

and the elimination of the conditioning discharges for increasing the deuteration factor (D-factor) of D/(H + D).

As the decaborane (B₁₀H₁₄) is easily ionized in the glow plasma and the boron is deposited on the first wall near the let-in port very quickly, the decaborane gas has to be delivered uniformly to get the homogeneous deposition of the films around the torus. Therefore, we increased the number of the ports to let in the process gas from only one to 12 around the torus. The homogeneity of the deposition has been improved; the deposition profile became uniform within a factor of 2.5 after adding the gas injection ports, while the thickness of the boronized layers had been ranging from 2 to 80 nm with only one injection port. The details will be shown elsewhere [9].

After the boronization using only He for a dilution gas, we needed ~ 500 discharges for exchanging hydrogen in the boron film for deuterium. We quote this type of boronization as He boronization hereafter. The H retention in the film has been analyzed to be H/B ~ 0.1 by an

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elastic recoiled detection analysis (ERDA). This hydrogen was released into the plasma and diluted the fuel particles. The D-factor $D/(H + D)$ in the first plasma just after the boronization was less than 0.2.

Therefore, we have to exchange the retained hydrogen to deuterium in order to realize D discharges. If we use the deuterated decaborane ($B_{10}D_{14}$) instead of $B_{10}H_{14}$, only the deuterium must be retained. In fact, B_6D_6 gas is used in DIII-D [5]. This procedure is ideal, however, the cost of these deuterated sources is so enormous that an advanced method has to be developed.

The He glow discharge decomposes $B_{10}H_{14}$ and the hydrogenated amorphous boron film is grown. Thus the origin of the H retained in the boron film is obviously the H atoms from the $B_{10}H_{14}$ molecules. Here, by changing the dilution gas from He to D_2 or the gas mixture of He and D_2 , the isotope exchange from H to D in the boron film will be accomplished due to the bombardment of deuterium ions on the H contained boron film. This type of boronization refers to deuterated boronization hereafter. This idea for the isotope exchange has been demonstrated in the laboratory experiments by Yamage et al. [10].

In this paper we describe the characterization of the boronized film which was made in the deuterated boronization in JT-60, comparing with those for the He boronization.

2. Boronization system

In JT-60, all of the plasma facing surfaces are composed of carbon tiles: carbon fiber composite (CFC) for the divertor plates and isotropic graphite for the all the other surfaces. A part of the CFC divertor plates are coated by B_4C [11]. Since 1992, boronization has been utilized seven times until now. The last two boronization sessions were deuterated ones.

The outline and the difference from the He boronization are mentioned here, because the details of the system were already described elsewhere [12]. The decaborane container and the delivery lines are heated to ~ 380 K during the boronization session, in order to supply a steady flow of decaborane gas and to prevent the decaborane from depositing on the surfaces of the delivery lines. First of all, dilution gas is made from blending He and D_2 , where by the flow rates of He and deuterium are independently controlled by mass flow controllers. Then, the dilution gas and the decaborane gas are fed continuously into the JT-60 vessel also independently controlled by flow controllers. The JT-60 vacuum vessel was evacuated by a $3 \text{ m}^3/\text{s}$ turbomolecular pump. The vacuum quality was monitored by a residual gas analyzer which was differentially pumped. Several kinds of monitoring system, which are sensitive to decaborane with the detectable concentration of as low as 10 ppb, are distributed at several points around the torus and the exhaust lines to ensure the safety.

The glow discharge was maintained in JT-60 using two graphite anode tiles spaced 140° apart toroidally, while the wall acted as the cathode.

The last boronization procedures were as follows. The He glow discharge cleaning was carried out for 10 h for cleaning the first wall prior to the boronization. At first the dilution gas was pure D_2 with the flow rate of 350 sccm, which corresponded to the pressure of 0.17 Pa. Here, the anode voltage was 420 V and the total anode current was 20 A. Then the $B_{10}H_{14}$ was allowed into the vacuum vessel, where the flow rate of the decaborane was 0.2 sccm. Supplying the decaborane into the vacuum vessel made the glow discharge very unstable. The discharge often vanished. Therefore, the dilution gas was changed to the gas mixture of He (50%) and D_2 (50%). The total flow rate of dilution gases was controlled at 420 sccm. The flow rate of decaborane was 0.2 to 1.2 sccm for the first 1.5 h, and was 2–4 sccm for the next 5 h. Above these rates of flow the glow discharge became unstable. Up to here, the consumed decaborane corresponded to be the boron film with the average thickness of 15 nm. Then we succeeded in increasing the decaborane flow rate to 6 sccm. And the ratio of the dilution gases was adjusted again for stabilizing the glow discharge. Here, the composition of the working gases was 2% $B_{10}H_{14}$, 38% D_2 and 60% He, which was used in a flow through situation. Total amount of consumed decaborane was finally 75 g, which was calculated to produce the boron film with average thickness of 200 nm. The vacuum vessel was heated to 523 K during the boronization.

Probes were located at two positions spaced 180° apart toroidally. Just after the boronization the samples were transferred and analyzed using several techniques (see below). The substrates of the probe were Fe and graphite, which were degassed at 923 K and 1273 K, respectively, for avoiding the uncertainty in measurements of the H and D retention.

3. Characterization procedures

The ratios of hydrogen (H) and deuterium (D) to the host (i.e. boron plus carbon) in the films were measured by ERDA, in which 30 MeV Ni^{9+} ion beam was incident on the specimens at an angle of 75° and detected 75° to the surface normal, respectively. In this case, the layer is completely analyzed. Therefore, the ratio of the constituents can be easily evaluated with high accuracy from the total number of counts ($\#A$ and $\#B$) for elements A and B, respectively, using the following equation [13].

$$A:B = \#A / \{Z_A(m_1 + m_A)/m_A\}^2 : \#B / \{Z_B(m_1 + m_B)/m_B\}^2, \quad (1)$$

where the notations Z_A (Z_B) and m_A (m_B) refer to the charge and mass of element A and B, respectively. The

incident beam has the mass of m_1 (in this case, $m_1 = 58$ amu).

There are five elements in the films on the Fe substrate: H, D, He, B and C. The ERDA spectra for H and D are energetically separated, while the recoil spectra for B, C and He are not decomposed (see Fig. 3). To use the Eq. (1), the counts for the host elements are calculated as follows:

(a) The contribution from He (#He) is subtracted from the couple (#N) of the counts of the 'B + C' and He, knowing where the higher energy side of He peak in the spectra appears and where the lower channel of carbon is located from the estimation of the energy loss of high energy Ni ions in the film with the thickness of 200 nm. Thus the count for the 'B + C' (#N - #He) is obtained.

(b) Furthermore, using the average carbon and boron quantity in the film from the depth profile measurements ($B:C = \alpha:1 - \alpha$), the counts for B and C are approximated as $\#B = (\#N - \#He)\alpha$ and $\#C = (\#N - \#He)(1 - \alpha)$, respectively.

Thus, from the Eq. (1), the ratios of the each elements are described as follows:

$$\begin{aligned}
 & H:D:(B + C) \\
 & = \#H / \{Z_H(m_1 + m_H)/m_H\}^2 : \#D \\
 & \quad / \{Z_D(m_1 + m_D)/m_D\}^2 : [(\#N - \#He)\alpha \\
 & \quad / \{Z_B(m_1 + m_B)/m_B\}^2 + (\#N - \#He)(1 - \alpha) \\
 & \quad / \{Z_C(m_1 + m_C)/m_C\}^2]. \quad (2)
 \end{aligned}$$

If necessary, the constituents for He, B and C can be obtained individually.

An upper limit for the error is neglectation of the He contribution in the ERDA spectra. For the data shown in Fig. 3, ratio of the count #He to the count #N is estimated as 0.14. This leads to the uncertainty of 15% for evaluating the H and D contents. Another factor for the error is uncertainty of the ratio of the host elements (B:C). Assuming the uncertainty of the value α to be 20%, retentions of the H and D have an error of 5%. Consequently, total error for the retention of hydrogen isotopes is 20%.

The elemental depth profiles were obtained by simultaneously eroding the surface with 3 keV Ar^+ ions and investigating the present chemical composition by a X-ray photoelectron spectroscopy (XPS) and a scanning Auger electron spectroscopy (SAM), respectively.

Moreover, the characterization of the film were studied using a secondary electron microscope (SEM).

4. Results and discussion

4.1. SEM observation before and after heat cycle

First of all, we examine the toughness of the film for heat cycle, because the boron and boron carbide film on

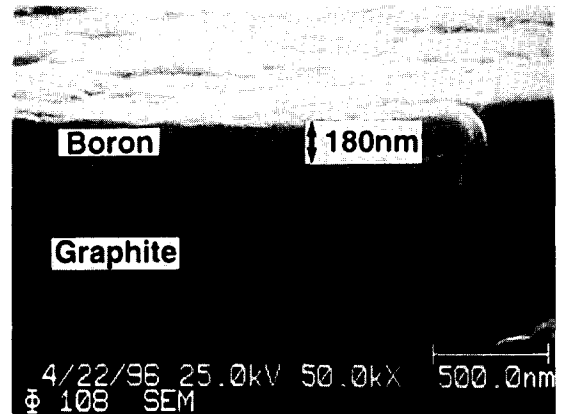


Fig. 1. SEM image of the cross section of the boronized probe sample. The substrate is isotropic graphite. The film thickness is 200 nm.

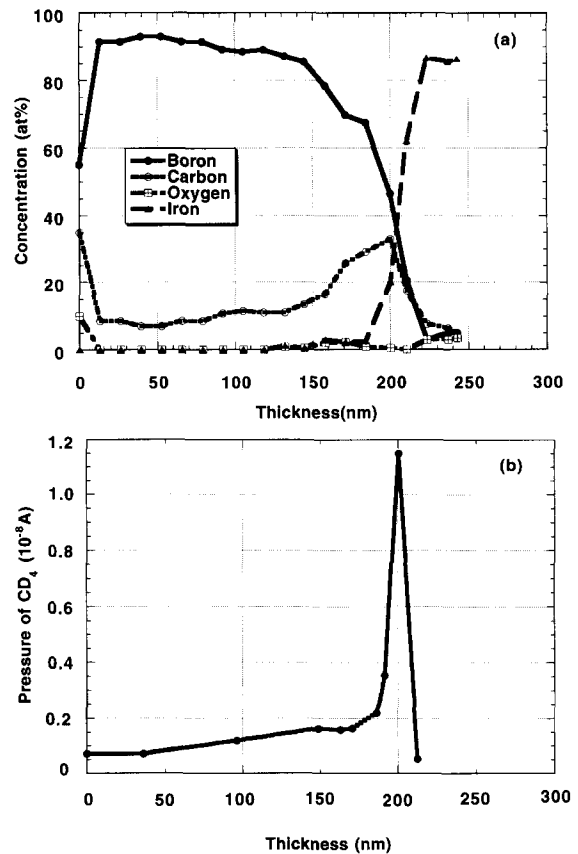


Fig. 2. (a) The depth profile for the deuterated boronization by XPS. A large amount of carbon (more than 10%) is contained in the film. Especially carbon near the interface is more than 30%. The oxygen level is very low. (b) The residual gas pressure of CD_4 during the deuterated boronization. Abscissa is shown as the depth from the surface after the boronization. The depth is calculated from the consumed decaborane as a function of time. The change in CD_4 pressure is well coincident with the carbon concentration in the film.

graphite or metal substrate, which are made by RF sputtering method, are likely to flake off easily [14]. We gave 5 thermal cycles to the boron films which was deposited on the collector probe. Then the cross section of the films were observed by SEM and SAM.

A thermal cycle consisted of heating from the base temperature (less than 323 K) to 973 K with the ramp up rate of 0.4 K/s and the cooling to the base temperature for about 1 h. The sample was heated at a pressure less than 10^{-6} Pa.

Fig. 1 shows the cross section of the sample after the heat cycles. The flake of the film was not observed when the substrate was cut off for the observation of the cross section. The adhesion is seemingly strong enough. The film thickness decreased during the heating from 200 nm to 180 nm. In addition, the observation by SAM revealed that the boron concentration in the film decreased and that the boron clearly extended into the graphite bulk. However, the details should be investigated in future.

4.2. Depth profile

The boron film made in He boronization had a boron concentration of over 98%. A small amount of carbon (less than 2%) and oxygen (less than 1%) was observed. Especially the oxygen was retained on the interface between the substrate and the film [7].

On the other hand, the depth profile in the film made in deuterated boronization is rather different, as shown in Fig. 2(a). The concentration of carbon is large. The maximum carbon concentration is 33% and exists near the interface. Then the carbon concentration decreases gradually to 10%

toward to the surface, while the boron concentration in the film is roughly 50% near the interface and then increases gradually up to 90% toward the surface. Finally the concentration of B and C is nearly constant above 150 nm from the interface up to the surface.

In the following, the origin of the carbon in the film is considered. It is not likely that the physical sputtering of the carbon wall is caused during the deuterated boronization, because the efficiency of the physical sputtering of D ions for carbon is less than that of the He ions and only little carbon is contained in the film made in the He boronization. More likely, chemical sputtering is the reason for the carbon in the film. Thus, the residual gas pressure of the CD_4 is monitored during the deposition process. The result is shown in Fig. 2(b). The abscissa shows the thickness which is measured from the surface after the boronization which is calculated from the consumed $B_{10}H_{14}$ quantity as a function of time. The carbon concentration in the film is similar to the CD_4 pressure. We conclude that the origin of the carbon in the film is CD_4 , which is formed on the graphite wall by atomic deuterium. This CD_4 is easily decomposed and the carbon is deposited on the probes as well on other parts of the first wall.

The production rate of CD_4 in the deuterated boronization session is likely to be explained as follows. At first the ratio of the D_2 to the He in the dilution gas increases. Therefore the production rate of CD_4 is higher in accordance with the atomic deuterium flux on the first wall. Then the pressure of CD_4 decreases gradually, because the larger area of carbon surface is gradually covered with boron and the surface area responsible for the methane

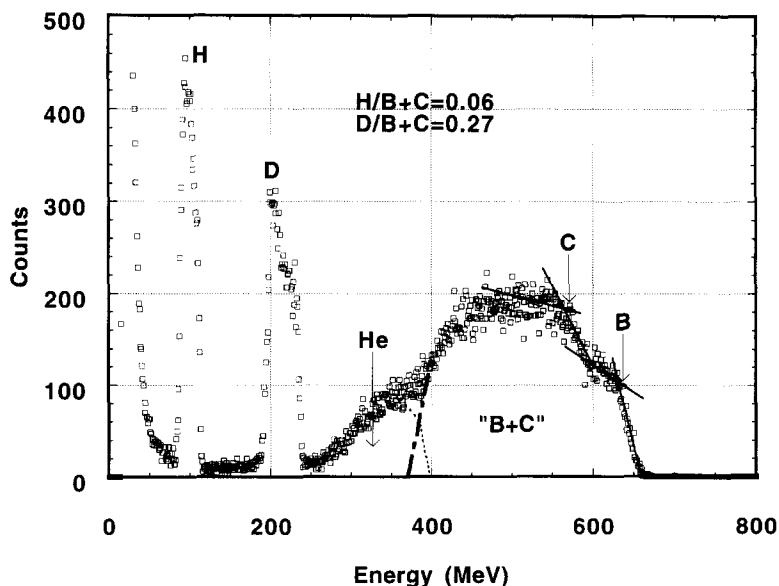


Fig. 3. The ERDA spectra for the film made in the deuterated boronization. The peaks of boron, carbon, helium, deuterium and hydrogen are shown.

formation decreases. Finally, the area facing the plasma is almost completely covered with boron and the atomic deuterium can interact only with the back surface of the first wall. Consequently, the production rate of the deuterated methane becomes constant.

4.3. Retention of H and D

The ratio of D to the total hydrogen isotope content (called 'D-factor') is a key factor for the deuterated boronization. Not only the retention of H and D but also D-factor was evaluated from the Eq. (2), using the ERDA spectra as shown in Fig. 3. The D-factors in the film are summarized in Table 1. We carried out deuterated boronization twice. For these two cases, the D-factor is over 0.8. The retention of H and D in the film for the 2nd deuterated boronization are $H/(B + C) = 0.06 \pm 0.01$, and $D/(B + C) = 0.25 \pm 0.03$, respectively, while the H retention in the film is $H/B \sim 0.1$ for the He boronization [7]. These data mean the deuterated boronization succeeds the exchange of hydrogen in the film to deuterium, although a rather large amount of hydrogen isotopes is contained in the film.

4.4. D-factor in the plasma just after the boronization

Finally, the D-factor in the plasma is investigated for the two kinds of boronization. To use observable data, we approximate the D-factor by the following equation:

$$\text{D-factor} = I(D_{\alpha}) / [I(D_{\alpha}) + I(H_{\alpha})],$$

where $I(D_{\alpha})$ and $I(H_{\alpha})$ refer to the intensities of the D_{α} and H_{α} lines of Balmer series from the near peripheral region of the plasma for deuterium and hydrogen, respectively. This approximation has been found to be effective for particle balance in JT-60 [15]. The results can be seen in Fig. 4. For He boronization, we need more than 100 discharges to obtain the plasma with a D-factor of greater than 0.8. In contrast, for the deuterated boronization the value of 0.8 is reached directly in the first tokamak discharges.

In the following, the relation between the D-factor in the film and in the plasma is discussed. Usually, the total number of ions in the plasma is $\sim 10^{21}$ ions in JT-60.

Table 1
Retention of hydrogen isotopes in the probe samples

	1st D-boronization ^a	2nd D-boronization ^a	He boronization
D/(H + D)	0.85	0.81	—
D/(B + C)	0.26 ± 0.02	0.25 ± 0.03	—
H/(B + C)	0.05 ± 0.01	0.06 ± 0.01	0.10
B:C	75:25	80:20	98:2

^a D-boronization refers to deuterated boronization.

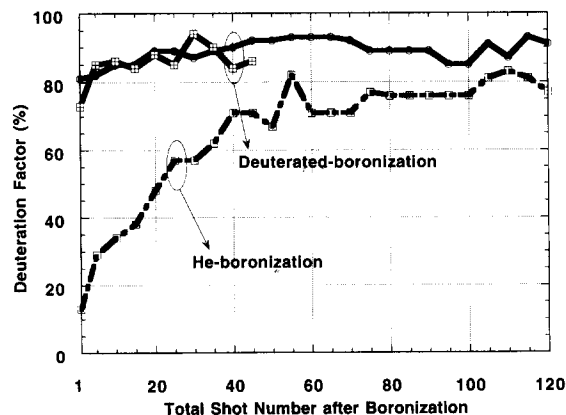


Fig. 4. The D-factor in the plasma as a function of the number of discharges just after the boronization. The D-factor after the He boronization is only 0.15, while the factor after the deuterated boronization is more than 0.8.

Because the confinement time of the particles in the plasma is ~ 0.1 s, total number of impinging particles into the plasma is $\sim 10^{22}$ atoms/s. This particle flux from the wall is about ten times larger than those from gas puff of $2\text{--}3 \text{ Pa m}^3/\text{s}$ ($\sim 10^{21}$ atoms/s). Therefore the D-factor in the film is responsible for the D-factor in the plasma. In fact, the D-factor in the film is nearly equal to the D-factor in the first plasma just after the deuterated boronization.

In JT-60, we usually start a D discharge with less than 10% H. Thus, we can drastically reduce the number of the discharges from ~ 500 to ~ 50 for the isotope-exchange before D plasma experiments.

5. Summary

The decaborane ($B_{10}H_{14}$) is easily decomposed and a hydrogenated amorphous boron film is grown with He as dilution gas in boronization procedure. By changing the dilution gas from He to the mixture of He and D_2 (called 'deuterated boronization') the isotope exchange from H to D in the boron film is accomplished.

The films as analyzed from the probe can be characterized as follows:

(a) The boronized films have enough adhesion strength to withstand the heat cycle from temperatures less than 323 K to 973 K.

(b) The boronized films in He boronization reaches a boron concentration of 95%, whereas films from deuterated boronization has a rather large amount of carbon (more than 20%). Carbon concentration near the substrate is higher than toward the surface. This is consistent with the production rate of the deuterated methane (CD_4). CD_4 seems to be decomposed in the glow and the carbon is deposited with boron.

(c) The deuteration factor ($D/(D + H)$) in the film is ~ 0.8 , while the factor in the pure He boronization is ~ 0.1 . Thus the isotope exchange from hydrogen to deuterium has been succeeded. This leads to the deuteration factor in the plasma being greater than 0.8 just after the boronization.

Acknowledgements

The authors would like to thank the members of JT-60 Facility Division II for the operation of the boronization facilities. In addition, they are grateful to Dr. M. Shimizu and Dr. A. Funahashi for their continuous support.

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