Hydrogen isotope trapping and retention in graphite and boron carbide under consecutive irradiation by deuterium and hydrogen plasma

A.A. Ayrapetov, L.B. Begrambekov, S.S. Dovganyuk, A.V. Grunin, A.S. Kaplevskiy, N.A. Puntakov
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)
31 Kashirskoe shosse, Moscow, 115409, Russia

E-mail: lexxair@plasma.mephi.ru

Abstract. The results of study on hydrogen and deuterium trapping and retention in MPG-8 grade graphite and boron carbide coating under consecutive irradiation by deuterium and hydrogen plasma in varying hydrogen irradiation conditions are presented in this paper. It is shown that deuterium content decreases both in graphite and boron carbide under irradiation by hydrogen plasma. It is also shown that the main mechanism of deuterium removal is sputtering for graphite, and isotope exchange for boron carbide.

1. Introduction
The problem of hydrogen isotope trapping and retention in graphite materials is important when considering their implementation as plasma-facing materials in thermonuclear facilities [1-4]. Uncontrollable desorption of hydrogen from graphite and graphite materials during plasma irradiation is of huge concern for such devices. Graphite has to be exposed to temperatures of about 800-900 K for prolonged periods of time for its thermal degassing. However, heating for such high temperatures is unacceptable for first walls of thermonuclear facilities. Degassing of graphite elements for devices using tritium poses a significant challenge, as the isotope becomes trapped in the plasma-facing elements, leading to the halt in operating the device and removing tritium from graphite elements.

One of the measures for protecting graphite materials is using renewable protective boron carbide (B₄C) coating [5-7]. Properties of boron carbide as a plasma-facing material are significantly different than those of graphite and other carbon-containing materials used in thermonuclear research. At the same time, accumulation of hydrogen isotopes in protective coating can negatively affect the device’s operation. Thus, studies on hydrogen isotope trapping and detention in graphite and boron carbide coating and the possibility of their removal are important.

2. Experimental facilities and methods
Samples made from full-body MPG-8 graphite with dimensions of 7x7x2mm³ were used in this work. The samples were consecutively polished using sandpaper with surface roughness of up to P2500 (ISO-6344 standard), washed in ultrasonic bath and annealed in the Multifunctional Investigation Complex for Mass Analysis (MICMA) [8] at temperature of 1450 K. A number of the samples were
coated with boron carbide coating 4-5 µm thick. Boron carbide coating was conducted on the Coating Deposition and Material Testing (CODMATT) stand [9,10] by depositing atoms sputtered from boron-carbon target by 10-12 keV energy argon ions on a sample.

Experiments on deuterium implantation, sample conditioning and hydrogen isotope trapping analysis were conducted on the “MICMA” stand. Residual vacuum in plasma chamber before discharge initiation was better than 2×10^-5 Torr. Deuterium implantation was done by irradiating the sample by D⁺ ions from gas discharge plasma. The discharge was initiated between the heated cathode and the anode. Anode potential was 150 V, discharge current was 1.6 A. Working gas pressure in the chamber during irradiation was 6×10^-3 Torr. Deuterium ion energy during irradiation was 100 and 650 eV/at., ion flux was 1.2×10¹⁶ at./cm²s и 1.6×10¹⁶ at./cm²s, respectively, fluences were ranging from 0,5×10¹⁹ at./cm² to 1×10²⁰ at./cm², sample’s temperature during the experiment was 630 K.

The content of trapped hydrogen isotopes and their thermal desorption spectrum was measured using thermal desorption spectroscopy (TDS) analysis in MICMA’s TDS chamber after irradiation in plasma chamber without exposition to atmosphere. The samples were heated during TDS analysis at a constant rate of 5 K/s in the temperature range of 300-1450 K. H₂, D₂ and HD molecules’ spectra were analysed (desorption of other hydrogen isotope-containing molecules was negligible).

3. Results and discussion
Preliminary experiments on measurement of trapped hydrogen isotope content under irradiation by deuterium ions at varying fluences were conducted to determine the fluence for the consecutive irradiation experiments. Saturation fluence for graphite was 7 × 10¹⁹ at./cm², trapped deuterium content was 1 × 10¹⁷ at./cm². For boron carbide, saturation fluence was equal to that of graphite, with trapped deuterium content being 1.55×10¹⁷at./cm². This implantation fluence was used in all consecutive experiments.

To determine the effect of hydrogen isotope emission on samples irradiated by deuterium under different conditions, a series of experiments was conducted with duration and temperature characteristic to that of hydrogen isotope plasma irradiation: exposition of the samples to vacuum and to hydrogen atmosphere at elevated temperature; irradiation of the samples by hydrogen atoms. These experiments showed absence of deuterium desorption from graphite under these conditions. Analogous experiments for boron carbide lead to insignificant decrease in trapped deuterium content after exposure to vacuum and to hydrogen atmosphere. Approx. 30% of deuterium trapped under ion irradiation is desorbed from boron carbide when the sample was irradiated by hydrogen atoms.

3.1. Hydrogen plasma irradiation of graphite
A series of experiments to determine the dependence of the efficiency of trapped deuterium removal with conditioning hydrogen discharge on irradiation fluence for two implantation energies (100 and 650 eV/at.) were conducted on graphite (Fig.1). For graphite with pre-implanted deuterium irradiated by hydrogen plasma ions with the fluence 0.5×10¹⁹ at./cm², deuterium content in the sample decreases and becomes 40-45% of initial value. The amount of trapped hydrogen, at the same time, increases by ~1.5 times. Deuterium desorption and hydrogen trapping continued, albeit with decreasing rates, until the maximum irradiation fluence was achieved. At the fluence of 3.5×10¹⁹ at./cm², deuterium content decreased to 19% of the initial value for the irradiation energy of 100 eV/at., and to 13% of the initial value for the irradiation energy of 650 eV/at., and the hydrogen content increased. Nevertheless, total amount of hydrogen isotopes trapped in the sample was less than the initial value. It is worth noting that after irradiation by hydrogen ions, deuterium content in the samples implanted at the energy of 650 eV/at. was higher (1.5×10¹⁶ at./cm²) than that for the samples with implantation occurring at 100 eV/at. (0.7×10¹⁶ at./cm²). However, the proportion of deuterium removed relative to the initial values is comparable for both samples. It can be assumed that desorption of deuterium trapped in graphite at other implantation energies would undergo analogously.
Increase of hydrogen irradiation energy to 100 eV/at. did not affect the value of deuterium left in the sample, or the desorption spectra. For altered values of ion flux density (from $1.5 \times 10^{15}$ at./cm$^2$/s to $7.5 \times 10^{15}$ at./cm$^2$/s), there was no change in the value of desorbed deuterium under the same fluence of hydrogen irradiation. The amount of deuterium desorbed increases twofold if the temperature is increased from 400 K to 630 K.

Deuterium removal from graphite under hydrogen ion irradiation can be partially due to sputtering of surface layer containing deuterium. Experiments were conducted to determine sputtering coefficient of investigated samples prepared using same techniques and under same conditions as the ones irradiated by hydrogen. Sputtering coefficient for hydrogen ion energy 50 eV/at., ion flux density $7.5 \times 10^{15}$ at./cm$^2$/s and sample temperature 630 K was 0.08±0.02. One can calculate that approx. 280±20 nm is sputtered under these conditions with the fluence of $3.5 \times 10^{19}$ at./cm$^2$, which is significantly higher than the characteristic depth of deuterium implantation. This explains the mechanism of deuterium removal from graphite under hydrogen ion irradiation: graphite layer, in which deuterium is contained, is sputtered by hydrogen ions. This assumption is confirmed by the matching of the dependences of deuterium desorption and graphite sputtering coefficient on ion flux density, ion energy and temperature. However, 15% of deuterium is still present in the sample even for irradiation fluence of $3.5 \times 10^{19}$ at./cm$^2$, which can indicate the intensification of trapped deuterium transport into the bulk of the sample under hydrogen ion irradiation.

![Figure 1](image-url)  
**Figure 1** Deuterium desorption from graphite and graphite with boron carbide after hydrogen plasma irradiation (hydrogen ion energy - 50 eV/at., temperature - 630 K, ion flux density - $7.5 \times 10^{15}$ at./cm$^2$/s), deuterium implantation ion energy - 650 eV/at.

### 3.2. Hydrogen plasma irradiation of boron carbide

Irradiation of graphite with boron carbide coating, implanted with deuterium, by hydrogen plasma ions with energy of 50 eV/at., ion flux density of $7.5 \times 10^{15}$ at./cm$^2$/s, and a fluence $0.5 \times 10^{19}$ at./cm$^2$, leads to the decrease in the amount of deuterium in the sample to 60% of the initial value (Fig.1). At the same time, the amount of hydrogen trapped is increased by ~2.7 times. With the increase of fluence to $3.5 \times 10^{19}$ at./cm$^2$, the amount of deuterium drops to 13% of the initial value, and the amount of hydrogen trapped increases. However, total amount of hydrogen isotopes left inside the sample is 30% lower than the initial value. With further increase of fluence to $7 \times 10^{19}$ at./cm, the amount of deuterium
in the sample becomes 9% of the initial value, with further increase in the amount of trapped hydrogen. At the same time, total amount of hydrogen isotopes is still lower than the initial value. Comparison of these experiments with analogous experiments on uncoated graphite shows that the effectiveness of conditioning of graphite with boron carbide coating is the same as for uncoated graphite.

Increase of hydrogen ion energy to 100 eV/at. does not affect the amount of deuterium left in the sample, trapped hydrogen and desorption spectra. The decrease of ion flux density (from 7,5×10^{15} at./cm^2 s to 1,5×10^{15} at./cm^2 s) lead to the increase of deuterium emission from the sample from 52% to 60% at a fluence of 0,5×10^{19} at./cm^2. With the decrease of temperature from 630 K to 400 K the amount of deuterium desorbed from the sample at the same dose decreased almost twofold.

It is known that sputtering coefficient of boron carbide in such conditions is lower than that of graphite for almost an order of magnitude, being 0,002 at./ion [11]. Thickness of surface layer sputtered by hydrogen ions with the energy of 50 eV/at. at a dose of 3,5×10^{19} at./cm^2 (∼5 nm) is significantly lower than implantation depth. Therefore, the removal of 87% of deuterium from the sample can’t be explained by sputtering. One has to admit that most deuterium atoms trapped in the surface layers of the coating, leave them and desorb due to isotope exchange unrelated to kinetic interaction between hydrogen and deuterium atoms. This is also supported by the fact that all the cases of removal of deuterium from graphite and boron carbide on coated samples was followed by the increase in hydrogen content by the same amount.

As such, the experiments conducted show that the application of protective boron carbide coating can allow removing trapped hydrogen isotopes from the material without its significant sputtering.

4. Conclusion.

It was shown in this work that exposition to vacuum, hydrogen atmosphere or hydrogen atom irradiation does not lead to desorption of deuterium implanted into graphite by plasma ion irradiation. A significant amount of deuterium desorbs from the graphite under irradiation by hydrogen ions. The main mechanism of deuterium removal from graphite is sputtering.

Exposition of graphite with boron carbide coating to vacuum and hydrogen atmosphere leads to insignificant decrease in implanted deuterium content; a significant amount of deuterium desorbs from the sample under irradiation by hydrogen ions and atoms. The main mechanism of deuterium removal from boron carbide coating is isotope exchange of deuterium and hydrogen atoms.

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References

[1] Skokov G., Sergeev V.Yu., Bykov A.S., et.al. 2014 Fusion Eng. Des. 89 Issue 12 P2816
[2] Melnikov A. V., Sushkov A. V., Belov A. M., et al. 2014 Fusion Eng. Des. 96–97 P306
[3] Nygren R.E., Youchison D.L., Wirth B.D., et.al. 2016 Fusion Eng. Des. 109–111 Part A P192
[4] Mendelevitch B., Boscarly J., Peacock A., et.al. 2015 Fusion Eng. Des. 98–99 P1235
[5] Begrambekov L.B., Buzhinskij O.I. 2007 Plasma Devices and Operations 15 № 3 P193
[6] Buzhinskij O.I., Semenets Yu.M Fusion Eng. Des. 1999 45 № 4 P343
[7] Buzhinskij O.I., Barsuk V.A., Otroschenko V.G. 2010 Fusion Eng. Des. 85 № 7–9 P1615
[8] Airapetov A., Begrambekov L., Bremond S., et al. 2011 J. of Nucl. Mater. 418 P1042
[9] Azizov E., Barsuk V., Buzhinskij O. et al. 2015 J.of Nuc. Mat. 463 P792
[10] Sadovskiy Y, Begrambekov L, Ayrapetov A, et al 2016 J. Phys.: Conf. Ser 748 012003
[11] Eckstein W., Garcia-Rosales C., Roth J., Ottenberger W. Sputtering data. IPP report 9/82 February 1993.