Introduction

Crystalline boron carbide coating $\text{B}_4\text{C}$, produced by a method of the chemical vapor deposition in a reactor from the fluoride phase at the temperatures up to $\sim 2000^\circ \text{C}$ has a number of substantial advantages before graphites: low chemical and physical sputtering, low ion-stimulated desorption and radiation-accelerated sublimation. As a result, a rate of the coating erosion and sputtering under ion and plasma irradiation in the up-to-date accelerating and thermonuclear facilities is much below, than for graphite. These characteristics vary a little up to the temperatures of $\sim 1400^\circ \text{C}$. Hydrogen capture in boron carbide is less in a few times, than in fine-grained, dense graphites and CFC composites. This difference is increased with an irradiation dose, hydrogen capture in $\text{B}_4\text{C}$ is saturated at doses about $10^{23}$ at/m$^2$. Boronization in-situ in a glow discharge results in to a formation of thin amorphous films of thickness up to 100 nm. Here a chemical sputtering, impurity atoms of carbon, oxygen and metals are suppressed. But such films are failing during several tens of plasma shots, therefore a boron deposition in a glow discharge is not very promising. Boron carbide films with a composition close to stochiometric $\text{B}_4\text{C}$ have been produced in the PISCES-B plasma with parameters similar to the DIII-D tokamak divertor plasma. Metacarborane $\text{C}_2\text{H}_{12}\text{B}_{10}$ was used as working substance. Deposition rate was extremely high $\sim 30$ nm/sec, that approximately in one thousand times exceeds a film deposition rate in a glow discharge. Thickness of deposited layer achieved of $\sim 40$ µm. The coating was the dense, hadn’t pores, had high hardness and good adhesion to a sample surface. It is of interest to research a production of boron carbide films in the tokamak plasma shots with higher parameters of density and electron temperature.

Experiments at tokamak T-11M

Boronization of the tokamak T-11M discharge chamber in plasma shots was carried out after experiments with lithium limiter. The placement of the lithium and graphite limiters, diagnostics, transport device with reference specimens and carborane container in the T-11M tokamak chamber is shown in Fig.1. Non-toxic and not explosive metacarborane ($\text{C}_2\text{H}_{12}\text{B}_{10}$) was used as working agent in boronization process. Electromagnetic valve was connected to a diagnostic port of the T-11M tokamak discharge chamber through a vacuum gate valve. The temperature of container ($T=20-150^\circ \text{C}$) was regulated by a thermostatically controlled heater.
Electromagnetic valve has been started from a tokamak toroidal field. Start time of its opening and closing could vary in a wide range. The plasma current was stabilized at 70 kA, toroidal field on axis was 11.5 – 12 kG. The deuterium and hydrogen mixture with ratio of H/D=1:1 was used in plasma shots. Behavior of the lithium, boron emission was defined by an optical method on the light intensity of neutral lithium and boron lines from near-surface plasma layer. Light emission intensity of the deuterium and hydrogen D-beta and H-beta lines was also measured from surface plasma layer. The electron temperature on a column axis $T_e(0)$ was uninterruptedly measured by means of two monitors of the soft X-radiation (SXR) with simultaneous measuring of plasma conductivity. $Z_{\text{eff}}(0)$ for various boronization conditions was estimated on plasma conductivity value. The five-channel microwave interferometer was used for measurement of electron density on different chords. Lithium limiter has moved away in "shadow" during an operation with a graphite limiter located at length of 20 cm from plasma centre.

**Plasma – carborane interaction**

Boronization in the T-11M tokamak was carried out after operation with lithium limiter without preliminary induction heating and cleaning of chamber by a glow discharge. In anterior shots (before boronization) atomic lithium, and also impurities came in plasma at the expense of ion sputtering from chamber walls. In Fig. 2a a plasma radiation spectrum before boronization is shown by red colour. There is a bright line of Li ion in plasma radiation spectrum. However, already after several shots with carborane Li line and impurities lines practically vanish from plasma radiation spectrum (Fig. 2a, black line), and B ion line appears. In the plasma radiation spectrum there are also deuterium and hydrogen lines. During lithium experiments, at approximately equal injection of deuterium and hydrogen into a chamber before plasma shot, D:H ratio in peripheral plasma was $\sim 1:1.3$. During boronization, at the same injection of deuterium and hydrogen into a chamber, D:H ratio in peripheral plasma changed up to $\sim 1:4$ (Fig. 2b, red line) at the expense of further injection of hydrogen, included in structure of carborane. B line disappeared from the plasma radiation spectrum (Fig. 2b, black line), when a valve for carborane injection was closed, D:H ratio became equal 1:2 (Fig. 2b, black line) and, simultaneously, lines of impurities have completely disappeared. The carborane injection valve has been opened at the most for 50 ms before the plasma shot start and start time of its opening could be varied in a wide range. Change of the valve opening time was well detected by optical diagnostics on the radiation spectrum of plasma shot. Time dependence of the B line intensity at opening of an injection valve for 50 ms before the plasma shot start (black line) and for 75 ms after shot start (red
Carborane injection during a plasma shot of the tokamak has improved a stabilization of a plasma column, and hydrogen recycling from the walls has decreased. The time dependencies of plasma current (a) and plasma density (b) along a central chord for carborane container temperature 100°C are presented in Fig. 4a, b. In Fig. 4c graphs of volts-seconds depending on a time are represented. As can be seen from figure, boronization results in an essential decrease of the volt-second consumption rate (and, correspondingly, to an increase of a shot duration). The time dependence of the hard X-rays detector indications is represented in Fig. 4d. Under boronization the hard X-rays intensity and radiation losses in plasma shot have decreased, and a plasma lifetime has increased almost in four times. Similar results for the carborane container temperature 50°C are represented in Fig. 5. Dependencies of a loop voltage before and after boronization are shown in Fig. 6, it is seen that a loop voltage of plasma column after boronization has decreased in two times. As a result of boronization in plasma shot, a boron-carbon coating has been formed on the polished substrate from AISI 321 stainless steel. The coating had a cellular structure. The size of cells in the centre of a sample is less than at the periphery. The coating thickness was defined by an optical microinterferometer MII – 4. In the centre of a sample the coating thickness was ~ 2000 Å, and at the periphery ~ 1200 Å. Boronization in tokamak plasma shots occurred during of about 50 impulses with total exposure time ~ 8 sec, thus a film deposition rate was ~ 25 nm/s. The film surface microhardness was measured by a microhardness meter PMT-3. The substrate microhardness was H<sub>10</sub> - 250, and a microhardness of the formed boron containing film H<sub>10</sub> - 600, that indicate on structuredness of the produced coating.

**Conclusion**

Experiments on boronization in the tokamak T-11M plasma shots using metacarborane were carried out. Stabilization of a plasma column has improved, hydrogen recycling from the vessel walls has decreased. Plasma shot duration without disruption has essentially increased, the hard X-rays intensity in plasma shot and radiation losses have decreased, a plasma lifetime has increased almost in four times. High repeatability of experimental results has appeared. The film with microhardness H<sub>10</sub> - 600 and the thickness up to 0.2 µm at deposition rate of ~ 25 nm/s has been produced as a result of boronization. The impurities in wall areas were suppressed, high vacuum characteristics of the discharge chamber have stabilized. Presented technology opens the possibility of practical production of renewable structured boron-carbon coating with use of plasma shots in large-scale tokamaks, such as T-15M, ITER, DEMO.

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Fig. 1. Location of diagnostics, limiters and carbonne container the tokamak T-11M.

Fig. 2a. Emission spectrum of T-11M tokamak plasma, before boronization (with lithium limiter) - shot 22641 and at the beginning of boronization – shot 22673.

Fig. 2b. Emission spectrum of T-11M tokamak plasma, during boronization – shot 22748 and without boronization – shot 22754.

Fig. 3. Time dependence of BIII line intensity at earlier (shot 22750) and later (shot 22753) start of boronization.

Fig. 4. Plasma shot parameters before, during and after boronization at boron containers temperature 100°C: a– plasma current, b– electron density, c– volt-seconds, d– hard X-rays.

Fig. 5. Plasma shot parameters before, during and after boronization at boron container temperature 50°C: a– plasma current, b– electron density, c– volt-seconds, d– hard X-rays.

Fig. 6. Loop voltage of plasma column in shots before, during and after boronization.