Boron carbide coating deposition on tungsten substrates from atomic fluxes of boron and carbon

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Abstract. A device used for both coating deposition and material testing is presented in the paper. By using lock chambers, sputtering targets are easily exchanged with sample holder thus allowing testing of deposited samples with high power density electron or ion beams. Boron carbide coatings were deposited on tungsten samples. Methods of increasing coating adhesion are described in the paper. 2 \( \mu \)m boron carbide coatings sustained 450 heating cycles from 100 to 900 C. Ion beam tests have shown satisfactory results.

1. Introduction
Currently, one of the main issues considering first wall materials of fusion devices is material erosion and dust generation [1-3]. First wall materials are being sputtered and codeposited layers are being formed. Protective boron carbide coating was proposed to prevent tungsten sputtering and consequent plasma contamination [4]. In a fusion device this type of coating could be deposited in-situ by using carborane vapors. In this case the coating would be formed of boron and carbon atoms originating from carborane molecules decomposition in plasma. For research purposes it is more convenient to deposit such coating by sputtering two separate targets made of boron and graphite and thus generating fluxes of boron and carbon atoms.

2. Boron carbide deposition on tungsten
Coating deposition as well as its consequent testing was performed on the CODMATT device (COating Deposition and MATerial Testing) [5]. Several modifications were done to the device prior to experimental program. The device could be easily transformed from deposition configuration to material testing configuration. Schemes of both configurations are presented in figure 1.

The device has one vacuum chamber (1) with a plasma chamber (2) inside. Two heated cathodes (3) and a ring shaped anode (4) on a motion feedthrough (5) are located inside the plasma chamber. The cathodes can be used independently or turned on simultaneously for higher emission. The device has two lock chambers – top (6) and bottom (7) equipped with gate valves (8) and special sealings (9) for motion feedthroughs. In deposition configuration the substrate (10) is introduced into the vacuum chamber on motion feedthrough (11) through the top lock chamber. The substrate is mounted on a copper table which could be biased in case the sample needs to be sputtered before coating deposition. The target unit consists of: a graphite cup (12), two anti-dynatron electrodes (13, 14) which connect with slip-contacts (15) when moved into correct position by motion feedthrough (16). A quadrupole mass-spectrometer with separate vacuum system is connected to the vacuum chamber through a leak.
valve. Thus it is possible to monitor working gas composition changes during coating deposition and sample testing.

A mix of graphite and boron powders and alcohol is prepared and applied on the surface of the graphite cup. This paste-like substance becomes solid crust when alcohol vaporizes. Graphite to boron powder ratio is 4:1 thus allowing the right stoichiometry of the coating.

Argon is used as a working gas. The device allows adding of hydrogen or deuterium to the working gas for the research of hydrogen trapping into coatings being deposited. Using of a heated cathode gives high control of the discharge current and thus plasma density. When high negative bias is applied to the target a ring-shaped ion beam is formed, exiting from the opening in the anode. Typical current and voltage values of the ion beam are 30-40 mA and 10-12 kV. Higher negative bias is applied to the anti-dynatron electrodes thus suppressing emission of secondary electrons from the target. Outer anti-dynatron electrode is made of tungsten and could be used a tungsten target in case source of tungsten atoms is needed for the deposition.

Figure 1. Scheme of the CODMATT device in two configurations: coating deposition (a), material testing (b). 1 – vacuum chamber, 2 – plasma chamber, 3 – heated cathode, 4 – anode, 5 – motion feedthrough, 6 – top lock chamber, 7 – bottom lock chamber, 8 – gate valve, 9 – motion feedthrough sealing, 10 – substrate, 11 – substrate motion feedthrough, 12 – target, 13 – outer anti-dynatron electrode, 14 – center anti-dynatron electrode, 15 – electric feedthrough, 16 – target motion feedthrough, 17 – sample being tested, 18 – copper table, 19 – testing table motion feedthrough.

Tungsten substrates of 15x15x1 mm size were used. The substrates were polished with sand paper of up to 2500 grade and then cleaned in alcohol in ultrasonic bath. Deposition regimes will be described below.

Deposited coatings were tested in various regimes with electron and ion beams. To allow this, the experimental device was reconfigured in the following way: the sample being tested (17) was fixed to a cooled copper table (18) which was introduced into the vacuum chamber through the bottom lock chamber similar to the target unit. The copper table is mounted on top of tube-shaped insulator and cooled with non-conductive silicon based fluid PMS-5 (poly-methyl-siloxane). This fluid is circulated in a closed loop with a heat exchanger which is in turn cooled by water. Using of a non conductive fluid allows direct cooling of metal parts which are biased with high voltage. The copper table was
designed to dissipate high power density heat loads and transfer heat from a small spot at the center of its top surface to a ribbed bottom surface actively cooled by the cooling fluid.

By varying the distance from sample table to the anode, value of the bias voltage and discharge current the shape of the ion beam could be changed as desired. By focusing the beam to a small spot one can achieve high power densities such as 20-40 MW/m². Total power of the high voltage supply is 4 kW. Without active cooling sample temperatures could be higher than 2000 K. Since the high voltage power supply is fully programmable, automatic thermocycling procedures could be performed. Pulse frequency could be as high as 100 Hz with independent control over duty cycle.

The polarity of the high voltage supply could be easily changed thus allowing electron beam irradiation. Thus one can compare ion beam and electron beam effects on the sample in almost identical irradiation conditions.

3. Deposition procedure optimization and testing of the coating.

Preliminary experiments have shown that when sputtering 4:1 boron and graphite powder mix coating composition is close to B/C=4:1. Coating composition was measured with Oxford Instruments X-Act EDS analyzer. Coatings with > 3 μm thickness had poor adhesion to the substrate, flakes were observed right after deposition. The deposited samples were tested both with pulse and stationary electron and ion beams. After the tests the surface was analyzed in TESCAN VEGA 3 SEM and in Quanta 200 3D FIB SEM, where a cross section of the surface was made by focused ion beam and depth structure was analyzed. Thus it was possible to observe delamination of the coating, pores and voids. The main characteristic of the coating adhesion was its ability to withstand pulse heat loads having certain maximum temperature with no flaking or cracks. Thermocycling tests up to 300, 600 and 900 °C were done to the samples deposited. Heating rate was 5 °C/sec.

First samples had 2 μm coating deposited at 200 °C with no interlayer. Massive flaking was observed on these samples already after 10 cycles with 300 °C maximum temperature. This result proves the need for special procedures intended for increasing coating adhesion to the substrate. In case of the ITER divertor, tungsten could play the role of the interlayer material. Thus, further experiments were focused on using tungsten as the interlayer material to increase coating adhesion.

The first stage included establishing of a smooth transition from substrate material to coating material. This method is common for increasing of coating adhesion. By mixing of materials in the interlayer there is no sharp border between different materials at which delamination can occur. Deposition procedure started with tungsten deposition on the substrate using outer anti-dynatron electrode as a target. Then bias voltages were varied constantly to smoothly decrease tungsten sputtering and at the same time start target sputtering. These voltages changes were preprogrammed in the high voltage power supply. Final bias values were the same as in previous experiments. Thus, an interlayer with ~200-300 nm thickness was deposited, establishing smooth transition from substrate to coating material. 2 μm coatings were deposited using this procedure. These coatings passed 100 thermocycles at 600 °C maximum temperature with no surface defects. When the maximum temperature of thermocycling was increased to 900 °C flaking was observed. Cracks in the coating often corresponded to cracks in the substrate. Crack sides were lifted off the substrate which is a sign of compressive stress in the coating. By analyzing the composition of the back side of a delaminated flake a conclusion about the layer of delamination was made. Tungsten content on the back side of the flake indicated that delamination occurred at the interlayer depth. Most probably, deposited tungsten was weakly bonded to substrate material.

Thus, at the next stage, substrate pre-sputtering was performed prior and during tungsten deposition. This serves two goals: cleaning of the substrate surface prior to deposition and mixing of substrate material with newly deposited material. The interface between substrate and deposited layer of tungsten is almost eliminated in this way. Then, the interlayer was generated as described above – smooth transition from tungsten to boron carbide. 2 μm coatings deposited in this way have sustained 450 thermocycles at 900 °C maximum temperature with no coating defects observed. Then, ion beam
tests were performed with the following parameters: H\textsuperscript{2+} ions with 6 keV energy at 0.5 MW/m\textsuperscript{2} energy density, pulse duration 100 sec. Sample temperature during this tests did not exceed 700 °C which is the temperature expected for ITER divertor tiles. After 120 such pulses sputtering artifacts were observed on the coating surface with no signs of flaking or cracking.

4. Conclusion
A multifunctional device allowing both boron carbide coating deposition and testing of materials and coatings with high heat and particle loads is presented.
A method of boron carbide coating deposition with good adhesion to tungsten was developed. This method could be realized in ITER conditions in-situ.
Deposited coatings sustained 450 thermocycles from 20 to 900 °C with no visible surface degradation. The coatings sustained pulse H\textsuperscript{2+} ion irradiation with 6 keV ion energy at 0.5 MW/m\textsuperscript{2} energy density and 700 °C maximum temperature with no cracking.

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