The possibility of boron carbide coating formation by using a coaxial magnetoplasma accelerator

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Abstract. A coaxial magnetoplasma accelerator can generate a dense and high velocity plasma jet by applying a pulsed high-current arc-discharge. The results of the experiment investigations of plasmodynamic synthesis in the B-C system have been shown while hyper speed jet boron carbide electric–discharged plasma steams onto copper substrate. The boron carbide coatings were formed on the copper substrate without a binder material. The formation of the crystalline boron carbide coating on the copper substrate was analyzed through X-ray diffractometry, transmission electron microscopy and scanning electron microscopy.

1. Introduction

Despite the superlative properties and the wide variety of potential applications of boron carbide, relatively little effort has been put. Boron carbide is one of the hardest materials. It has a high melting point, high resistance to chemical agents, low density and lightweight. It can be applied in many areas as abrasive powders and coatings, in nuclear applications as neutron radiation absorbent, ceramics, an impurity in thermoelectric device material and etc. [1].

As a result of these boron carbide properties there is an interest not only in powder, but also in coating, which can be used as protective layer from aggressive environments and high temperatures in different units. One of the most perspective investigations in that sphere is obtaining thick boron carbide coatings (300-500 µm) for tokamak wall in nuclear fusion reactor. The most popular method for obtaining such coatings is vacuum plasma deposition method.

B₄C can be prepared by several methods, such as laser assisted CVD, microwave CVD, filament activated CVD, sputtering and radio-frequency plasma CVD. Most of these methods have a number of disadvantages, such as process duration, coatings thinness, low adhesion, necessity of high temperatures and energy intensity as a result [2].

2. Experimental

Plasmodynamic method is a possible way of sintering boron carbide phase avoiding above mentioned problems. The method is realized on the basis of the pulsed high-current coaxial magnetoplasma accelerator [3]. The dominant part of the precursors is acquired by accelerator channel erosion due to high velocity of the plasma jet.

Powder-like electro conductive precursor compound is consisted of a black amorphous boron and amorphous carbon. Their ratio is 4:1 and total mass is 1.0 g. That precursor material is put into plasma forming structure area. It acts as electro conductive wire providing arc discharge initiation between graphitic central electrode and graphitic accelerator channel (AC) surface at the beginning. The
cylindrical AC diameter is 9.5 mm and length is 150 mm. Power source of CMPA is obtained from a capacitor, which has volume of $C=6 \, \text{mF}$. Charge voltage is about 3 kV. The plasma discharge is produced in chamber-reactor at room temperature. The chamber-reactor is filled with argon at 1 atmosphere. The volume of the chamber-reactor is 0.002 m$^3$. These dimensions are not fixed and can be changed if there is necessity.

The energy parameters of the CMPA operational cycle are plotted in the form of voltage and current oscillograms, power and energy consumed curves in Fig.1.

![Figure 1](image_url)

Figure 1. The typical oscillograms of the impulse current $I(t)$ and voltage $U(t)$ of the coaxial magneto plasma accelerator electrodes, the power discharge $P(t)$ and energy curves $W(t)$.

By applying a high discharge current of roughly $10^4-10^5 \, \text{A}$ the temperature of the order of $10^3 \, \text{K}$ can be achieved between graphitic electrodes, in the limited volume of the AC, causing evaporation or initiating chemical reactions. Conductive induction electrodynamics force in a coaxial system and gas-kinetic pressure in the aggregate allow achieving on the section of the AC the velocity of the bow shock wave of supersonic plasma jet that equals about 2 km/s. The chamber-reactor opening is performed after approximately 1 hour of the plasma shot. As a result, occurs full deposition on the walls of the ultrafine synthesis product fraction.

3. Results and discussion

Analytical data of the sintered samples are received by the following methods without any preparation: X-ray diffraction (XRD) (diffractometer Shimadzu XRD 7000, 0.15406 nm); scanning electron microscopy (SEM) (Quanta 200 3D microscope and Hitachi TM3000); transmission electron microscopy (TEM) (microscope Philips CM12).

Significant reduction of amorphous carbon fractions and pure crystalline carbon phases is obtained by halving the total weight of the sum compound of the precursors to 0.5 grams. But the ratio of the precursors is the same thus precursor powder contains 80 wt. % boron and 20 wt. % carbon.
In the Fig. 2a an obtained powder is presented. As seen in the Figure 2b, the most part of the plasmodynamic synthesis has deposited on the copper substrate in the form of bulk gray material. The character of deposition and dispersion on the surface indicates that the product has turned into a liquid state and crystallized due to quick cooling. Thus gas phase precursors that have been dissociated to form molecular fragments which condense to form thin film.

![Figure 2. The chamber-reactor walls powder photograph (a) and the boron carbide coating on the copper substrate (b).](image)

The outer surface of the deposited material and the surface of adhesion with the surface of the copper substrate have been analyzed by the XRD method. Practically identical XRD – patterns have been obtained. Fig. 3 shows the diffraction pattern taken from a front side of the deposited bulk material.

![Figure 3. The XRD pattern of the boron carbide coating.](image)

The strongest XRD-reflections of crystalline copper are in the figures because of its higher density as compared with boron carbide. In addition the crystalline boron carbide reflexes are in the XRD patterns. Fig. 4 shows the SEM images in detection mode, back scattered electrons, giving contrast material density. In the overview photograph (a) at low magnification x1000 surface irregularity of the bulk material precipitated is visible.
Figure 4. SEM images of the boron carbide coating. The right side of the coating (a); the element analysis data (b) of right side of the coating; the right sides of the coating (c), (d); the backside of the boron carbide coating (e); the elemental analysis of the backside (f).

Large gray contrast areas, mainly consisting of low density material, as well as areas with granular surface structure, mainly consisting of high-density material, are clearly distinguished. SEM images of fragments of these regions with magnification x10000 (c) and x5000 (d) allow concluding that in both areas the solid coating is a composite. Its basis is gray or very dark grains with geometrically irregular shapes of low-density material being in the matrix of the high-density material. In gray areas contrast (Fig. 4c) reveals grains in light matrix more closely, and their material can prevail over the light matrix material in volume and weight. In the second case (Fig. 4d) the structure with matrix material dominance takes place. Fig. 4b shows energy dispersive analysis of the surface and it gives the integral content of elements shown in Fig. 4a. The energy dispersive analysis results conform well to the visual assessment and X-ray analysis of the deposited bulk material results.

The layer thickness of the material is not uniform and does not exceed 100 microns on average. Besides XRD pattern of the back-side contacting copper substrate is identical to the coating diffraction pattern (Fig. 3). However, as shown in Fig. 4e, the material of the back-side substrate is low density and porous. The data of the energy-dispersive analysis of the front and back surfaces of the sample reflecting the integral ratio of the elements are presented in Fig. 10b, f.
It is seen that on the front surface there are about ~ 40% of copper and about 60% of the B-C material in the ratio which is close to B13C2 stoichiometric boron carbide. On the back side the copper is practically absent in the material of the gray contrast. And the copper content is about 3.0% presumably due to the presence of very large fragments peeled off from the copper surface. Dominant B-C material has also the ratio of elements close to the stoichiometry of the boron carbide B13C2.

Fig. 5 shows a precipitated material cross cleavage separated from the copper substrate. On the border with the copper substrate uniform layer of gray material is visible, which is boron carbide. Above this layer a composite layer of boron carbide and copper is formed. Such distribution of the main phases of the bulk material thickness can be interpreted as follows. Boron carbide is synthesized in the discharge plasma in the accelerating channel at a high temperature. After that liquid state boron carbide is carried out of the AC and covers still "cold" surface of the copper substrate. The temperature of the liquid state boron carbide is not less than 2350 °C, which is considerably higher than the melting point of copper. The surface of the copper layer melts by a large temperature gradient meanwhile the carbide melt temperature decreases and the crystallization starts with the formation of solid carbide layer ejecting still hot copper melt to the surface layers. While it is cooling due to heat shrinkage the layer is cracking and dividing into a geometrically irregular grain shapes. In microgaps formed between the grains by capillary action comes copper, which is still in a liquid state, and is in near-surface micro-layer of material layers. The composite material is formed.

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5. Summary
Thus, this scheme of supersonic jet electro plasma sputtering on the substrate allows forming a coating based on boron carbide. Low adhesion is due to the high degree of crystallinity and a low temperature substrate [4].

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