Group growth of polycrystalline diamond coating by MPCVD technique on a hard alloy tool with a thin blade

E E Ashkinazi¹,²,⁶, A F Popovich¹,³, V Yu Yurov¹,², V S Sedov¹,², D N Sovyk¹,², K F Sergeichev¹, V E Rogalin¹ and V I Konov¹,²

¹Prokhorov General Physics Institute, Russian Academy of Sciences, 38 Vavilov str., Moscow, 119991, Russia
²National Research Nuclear University MEPhI, 31 Kashirskoe highway, Moscow, 115409, Russia
³V. A. Kotelnikov Institute of Radio Engineering and Electronics RAS, 1 Vvedenskogo sq., Fryazino, Moscow Region, 141190, Russia
⁴Tver State University, 33 Zhelyabova str., Tver, 170100, Russia

E-mail: ⁶jane50@list.ru

Abstract. A coating technology for application of hardening of diamond coatings on carbide tools for treatment of mineral fiberglass based on quartz texture with chromate-phosphate cohesive (FQTCC) is proposed. The purpose of this development is to increase the edge strength of the tool. The use of the technology described above allowed, in comparison with the cutter without diamond coating, to increase the productivity of processing by 11.5 times, by cutting speed by 2.3 times, and by the minute supply by 5.0 times. The approach is based on changing the configuration of the microwave field when applying a diamond coating on hard alloy substrates in the microwave plasma of the ARDIS-100 reactor by using specially designed plateholders. This method allows for the group coating on several substrates in a single process. A simplified mathematical model for calculating the temperature of the top of the cutter during the growth of a CVD diamond film, taking into account heat transfer through thermal conductivity and radiation, has been constructed. Temperature distribution on the surface of a tungsten carbide cutter in the temperature range optimal for diamond growth was constructed. The difference between the average (experimental) and maximum (calculated) temperature in such a cutter was from 80 to 138°C.

1. Introduction

When coating of carbide or hard alloy tools with diamond films to process composites, one has to solve a number of problems. Chemical vapor deposition from microwave plasma (MPCVD method) allows to obtain high-quality homogeneous CVD diamond coatings and films [1, 2]. However, if a cutter of hard alloy is placed on an open substrate holder, anomalous effects appear, including so-called “edge effect”, due to plasma concentration irregularities and thermal phenomena near the edges of the sample [3]. Both temperature and grain size of polycrystalline diamond films increase sharply at the hot edge. The edge effect occurs at the cutting edge preventing the diamond growth due to its overheating. The use of a movable coaxially ring (shielding ring) around the cutters or plates located in the center of the CVD chamber allows to minimize the edge effect [4]. The microwave plasma (MW) is confined to the shielding ring, and thereby, the interaction of the plasma with the cutter edges weakens. In this case, the
cutters inside it are predominantly heated by radiation. By adjusting the vertical position of the ring, it is possible to control the intensity of the interaction of the plasma with the cutter surface and to find the optimal deposition temperature without changing other process parameters.

In this work, Tungalloy cutters (WC-Co where Co concentration is 3% w.) with a wedge-shaped tip protruding at an angle of 60° to the body were subjected to MPCVD to study the effect of heating by MW plasma cloud of the cutting edge and cutting tip of the carbide tool. The solution of the thermal problem of the cutter top overheating in MW plasma was made by the finite element method in the AutoCad, 3D program.

The morphology and quality of the diamond coating was evaluated using both SEM and practical tests on milling of composite materials made of FQTCC with diamond coated cutters.

2. Experimental technique
Diamond coating was synthesized in “ARDIS-100” MPCVD system manufactured by Optosystems Ltd. (2.45 GHz, 5 kW) as a result of decomposition of CH₄ / H₂ / N₂ gas mixture into radicals, mostly hydrocarbons (CHₓ) and atomic hydrogen (H) [4] in the reaction chamber. The growth conditions were as follows: MW power of 3.15 kW, gas pressure of 60 Torr, substrate temperature of 800°C, gas flows of CH₄ / H₂ / N₂ were 20 / 480 / 0 sccm to grow microcrystalline diamond (MCD) film. After 2.5 hours of such deposition, the gas flows were changed to CH₄ / H₂ / N₂ of 20 / 460 / 20 sccm without changing other parameters to grow nanocrystalline diamond (NCD) layer on top of the MCD film with growth duration of another 2.5 hours. The final thickness of the diamond film reached 12 µm.

To remove cobalt from the hard alloy plates, the method of step-by-step chemical treatment of the substrate with Murakami’s reagent and Caro acid was used [4]. The barrier layers of tungsten (W) were deposited with preliminary ion addition, consisting of two stages: 1) deposition of a thin (10÷30 nm) tungsten underlayer on the substrate activated by the ion beam at a magnetron discharge working pressure of less than 0.25 Pa; and 2) the subsequent film growth at optimum pressures of 0.5÷0.7 Pa [3]. The isotropic structure preserved up to 600 nm thickness.

The substrate temperature was controlled using a dual-band IR pyrometer (“Williamson”, model PRO-81-35-C). The pyrometer recorded the temperature of the edge of the diamond coating (the spot diameter was approximately 2 mm). After carrying out the process, the surface morphology of the sample was monitored by a scanning electron microscope (SEM) JSM-6510LV (JEOL). Comparative tests of hard alloy plates with a CVD-diamond coating 12 µm in thickness were carried out on a 3-axis CNC machine VM 12-500 during the operation of milling of a composite material made from FQTCC.

3. Results and discussion
Thin blades of hard alloy tools, mounted on replaceable plates of milling cutters, are effectively used in the processing of modern composite materials. Their cutting edges protrude 1/3 of the height of the cutter body, and the blade sharpening is determined by the difference of angles between the back and front surface, which, as a rule, exceeds 11° and (−)30°, respectively [5]. Overheating of the cutter in the area of the thin blade during the growth of the diamond film on the FOTCC negatively affects the quality of the grown film adhesion to the substrate, contributing to the diffusion of cobalt into the nucleation zone of diamond carbon [6]. It is known that the temperature of diamond deposition on flat substrates can be controlled by changing the distance Δh between the surface of the shielding ring (plateholder). The substrate is placed in the plateholder cavity, and the deposition temperature can be changed without changing other growth parameters (power, pressure etc.). If the substrate is higher than the shielding ring (Δh> 0), the temperature rises; if the substrate is located below the ring (Δh <0), the temperature decreases. Automatic control of the Δh parameter allows to control the substrate temperature in situ [4] without altering other process parameters.

A thin blade protruding above the substrate body complicates the temperature measurement procedure due to its shape, size, and distortion from the radiation of the microwave discharge plasma. The Williamson infrared pyrometer aimed at the side surface of the sample through the side window of the CVD reactor chamber was used to measure the temperature of the samples during growth in the
CVD reactor [4]. If the pyrometer is located above the sample, so that its optical axis is located vertically or at a small angle to the vertical, significant radiation from the microwave plasma arrives at the input of the pyrometer, which certainly distorts the measured sample temperature. The location of the pyrometer on the side of the camera and registration of radiation from a sample propagating horizontally to the side avoids parasitic plasma illumination and improves the accuracy of temperature measurement. A prerequisite for group growth of diamond coating in a microwave plasma reactor is the determination of the critical size of the internal diameter of the ring, within which the vertical electric microwave field cannot propagate and fades out exponentially.

It is known that the temperature measured by the pyrometer strongly depends on the emission coefficient of the sample (for the single-range mode) or on the ratio of the emission coefficients in the two working ranges (for the dual-range mode). Therefore, in order to calibrate the pyrometer for correct temperature measurement, lateral surface of the hard alloy cutters was preliminarily coated with a black polycrystalline film having a high absorption coefficient and emissivity in a wide range of wavelengths. In this case, the ratios of radiation coefficients in the two working ranges of the pyrometer were close to 1. The emissivity of the polycrystalline diamond deposited on the hard alloy substrate was tested in a vacuum furnace equipped with a calibrated Pt/Pt+10%Rh thermocouple (S-type) with an accuracy of ±5°C. The working vacuum in the furnace was 2x10⁻⁵ Torr, which excluded the chemical interaction of oxygen with the diamond film and kept its emission properties unchanged when heated to 1200°C. The vacuum furnace was equipped with a window for measuring the temperature of the samples with a pyrometer, so the pyrometer readings could be compared with the thermocouple readings. As a result, it was found that the ratios of emission coefficients of the diamond film on the WC-Co substrate in two Williamson pyrometer operating ranges was 0.98, which made it possible to further measure the temperature of the cutters in the CVD reactor only with a pyrometer with an accuracy of ± 30°C.

The solution of the thermal problem of heating the hard alloy cutter in microwave plasma was obtained on a simplified model in the program “AutoCad, 3D”. To calculate the thermal field, the following simplifications were introduced in the model: the substrate surface was heated by radiation and thermal conductivity of the gaseous medium from a heater (MW plasma), located at a distance of 5-10 mm from the cutter surface and the shielding ring; convection heat transfer was not taken into account due to the low pressure in the microwave reactor (0.1-0.3 atm). The temperature of the bottom surface of the molybdenum base, on which all elements were placed, was kept constant from 200 to 500°C. The scheme of the mutual disposition of the mentioned objects of the model and its splitting into finite elements is shown in Figure 1. Further, in the “Ansys” program, the stationary thermal problem was solved and the results were analyzed to select the optimal growth conditions at the upper surface of a tungsten carbide cutter.

It can be seen from the model (Figure 1, on the right) that the temperature of the front surface of the cutter is not uniform in height. The top has a negative rake angle γ and is located on elevation. It has the higher temperature than the other parts. Direct measurements of the temperature of the cutter top with a pyrometer are possible only through the upper window of the reactor. In this case, the background illumination of the microwave plasma between the substrate and the pyrometer prevents correct measurements. The simulation used experimental data obtained by measuring the temperature in the side, in the middle of the substrate, through the side window of the reactor. The measured heating temperatures correspond to the different position of the substrate in the resonator of the microwave reactor, and they are in the range from 620 to 969 °C. The calculated temperatures of the top of the cutter for these values are presented in Figure 2. For each curve, the calculated temperature for the top of the cutter (maximum, rightmost) and experimental (pyrometer) temperature for the middle part are given.
Figure 1. General view of the simulated installation and materials of particular elements, used in the simulation – on the left; the distribution of the thermal field in the cutter (WC-Co) – on the right.

Figure 2. A series of temperature curves of the top of the cutter, obtained by simulation, at different power of the heating source. The maximum temperature corresponds to the heating of the cutter top, the point of intersection of the curve with the dotted line is given by the experiment.

It was experimentally found [4] that the restriction of the central region of the base conductive platform of the reactor, by the conductive ring placed on it, equalizes the growth conditions of a flat substrate, in particular, the temperature distribution on its surface. The influence of the ring on the microwave field distribution is favorable for the diamond growth in the plasma inside the ring if the ring radius is less than the critical radius of a circular waveguide for wave type $E_01$ for a given frequency of 2.45 GHz.

A metal ring lying on a conductive base is a short circular waveguide that is excited by a vertical electric microwave field. Inside the ring, the external microwave field in the direction of the axis cannot propagate and decays exponentially. In this case, the phase coefficient in the ideal waveguide $\beta=0$, i.e. the field does not change with the height of the ring in phase, and the attenuation coefficient of the field amplitude $\alpha$ is determined by the formula:

$$\alpha = \frac{2\pi}{\lambda} \sqrt{\frac{\lambda^2}{\lambda_c^2} - 1},$$  \hspace{1cm} (1)
where $\lambda$ – the wavelength in free space, $\lambda_c$ – the critical wavelength of type $E_{01}$, which is determined by the radius $R$ of the waveguide (we consider it to be an empty dielectric):

$$\lambda_c = \frac{2\pi}{\nu_{01}} R = 2.61R,$$

(2)

Here $\nu_{01} = 2.405$ is the radical of the Bessel function. The attenuation of the amplitude of the wave $E_0$, excited at the edge of the waveguide, will be:

$$E = E_0 \exp(-\alpha z)$$

(3)

Let us calculate the attenuation of the field of the wave $E_{01}$ inside a ring of radius $R = 3.5$ cm lying on the plane in the center of the reactor for the operating frequency of 2.45 GHz with a wavelength of $\lambda = 12.24$ cm:

$$\lambda_c = 2.61 \times 3.5 = 9.135$$

$$\alpha = \frac{2\pi}{12.24} \sqrt{\left(\frac{12.24}{9.135}\right)^2 - 1} = 0.458$$

Suppose that the ring height $z = 0.6$ cm. On a plane inside the ring, the field will decrease to the level:

$$E = E_0 \exp(-\alpha z) = \exp(-0.275)E_0 = 0.76E_0, \text{ accordingly, } E \text{ will decrease to 57\%.}$$

The ring is filled with plasma which shifts the refractive index of medium $n$ in the direction of decreasing. This makes it possible to bring the inside diameter of the ring to its critical size of 90 mm, since the wavelength in plasma becomes larger than in vacuum. Hard alloy cutters with average size of 12×7 mm, being placed inside such ring, can be covered with CVD diamond realizing group growth of up to 50 cutters simultaneously.

The structure of the samples was examined by SEM using a microscope “JEOL JSM-6510LV” (Figure 3).

The cutting edge of the diamond coated WC-3%Co cutter has a thickness of about 14 μm (Figure 3b). Polycrystalline diamond morphology is typical for nanocrystalline films grown with a relatively high methane content in a mixture of CH$_4$ / H$_2$ / N$_2$: cauliflower-type globules with a diameter of 2.2-4.5 μm, consisting of needle-shaped diamond crystallites with a diameter of 0.2-0.4 μm and a graphite-like shell covering them (figure 3d). This nanocrystalline film consists of streamlined globules with a size of actually single diamond grains of less than 0.4 microns (Figure 3). Whereas for a common microcrystalline film of comparable thickness – about 10 μm – the size of diamond crystallites is 2-3 microns, and, what is more, they are faceted with sharp edges, formed by the (111), (110), (100) and higher crystallographic indices. The advantages of a nanocrystalline diamond coating over a microcrystalline are low roughness, depending weakly on the film thickness, and, consequently, low friction coefficient and long cutting/turning length [5].

Comparative tests of a 16 mm end milling cutter equipped with hard alloy cutters with our CVD diamond coating were carried out at the milling operation of composite material FQTCC on a 3-axis CNC machine VM 12-500. As a result, a milling cutter with the CVD diamond coating, when machining KM FQTCC with a cutting depth of $t = 1$ mm, provides the required quality of the treated surface at increasing the rotational speed of the cutter from 4400 rpm to 10000 rpm, as well as by increasing the minute feed of the milling cutter from 440 mm / min to 2200 mm / min. Thus, it was possible, in comparison with the cutter without diamond coating, to increase the processing performance by 11.5 times, cutting speed by 2.3 times, and the minute feed by 5.0 times.

The electron microscopic image of the wear of the top of the hard alloy cutter with CVD diamond coating after the tests and cross-section of WC + W + CVD diamond film are shown in Figure 4. It can be seen that at the top of the cutting plate, the film did not peel off from the hard alloy WC-3% Co. As a result of the milling tests, there was a uniform removal of all the material: a diamond film, a tungsten underlayer and a hard alloy. The coating is characterized by high adhesion to WC-3% Co even at the most problematic point – on the top of the cutting plate. Removal of material exposed the structure of WC-3% Co. One can see cubic, octahedral tungsten carbide grains with the size of 0.3-1.2 μm which
are 4 times larger than the grains of the NCD film located above (Figure 4). The second most important reason for high adhesion of the coating is reducing the size of crystallites, besides the optimal conditions of heating the WC-3% Co substrate during microwave plasma CVD of diamond.

Figure 3. SEM micrographs of the elements of a thin blade of the cutting edge of a hard alloy WC-3% Co cutter with CVD diamond coating. The morphology of the MCD/NCD film on the cutting edge (a, b) and on the front surface of the cutting edge of the MCD/NCD diamond layer (c, d).

Figure 4. SEM micrographs of the wear at the top of the WC-Co cutter and the CVD diamond coating (left) after milling the FQTCC, the cross- section of WC + W + CVD diamond film is shown with the arrow (right).
4. Conclusion
1. A simplified mathematical model was built for calculating the temperature of the top of the cutter during the growth of CVD diamond film. This model takes into account heat transfer through thermal conductivity and radiation.

2. The temperature fields on the surface of the tungsten carbide cutter in the temperature range that is optimal for diamond growth were built.

3. The difference between the average (experimental) and maximum (calculated) temperature in such a cutter was from 80 to 138°C, increasing with the growth of the power supplied to the model under study.

4. The use of the technology described above has allowed to increase the processing performance of FQTCC by 11.5 times, cutting speed by 2.3 times, and the minute feed by 5.0 times, in comparison with the cutter without diamond coating.

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References
[1] Wild Ch, Herres N and Koidl P 1990 Texture formation in polycrystalline diamond f. J. Appl. Phys. 68 973–978
[2] Gritsyna V I, Dudnik S F, Koshevoi K I, Opalev O A and Strel’ntskij V E 2013 Synthesis of high-quality diamond coatings by methods of activated chemical vapor deposition PSE 11(1) 63-77
[3] Fernandes J S A, Silva V A and Rodrigues Dias J M C G 2001 MPCVD diamond tool cutting-edge coverage: dependence on the side wedge angle Diamond and related materials 10(3) 803-808
[4] Ashkihazi E E, Sedov V S, Sovyk D N, Khomich A A, Bolshakov A P, Ryzhkov S G, Khomich A V, Vinogradov D V, Ralchenko V G and Konov V I 2017 Plateholder design for deposition of uniform diamond coatings on WC-Co substrates by microwave plasma CVD for efficient turning application Diamond and related materials 75 169-175
[5] Karpat Y and Polat N 2013 Mechanistic force modeling for milling of carbon fiber reinforced polymers with double helix tools Manufacturing Technology 62(1) 95-98
[6] Polini R, Barletta M, Rubino G and Vesco S 2012 Recent advances in the deposition of diamond coatings on Co-cemented tungsten carbides Advances in Materials Science and Engineering 151629