

## Microwave CVD Deposition and Properties of Nano / Microcrystalline Diamond Multilayer Coatings on Tungsten Carbide Cutting Tools

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**Abstract**—Micro/Nanocrystalline multilayer diamond coatings (DC) were produced using a microwave plasma-assisted CVD process from  $\text{CH}_4/\text{H}_2$  (microcrystalline) and  $\text{CH}_4/\text{H}_2/\text{N}_2$  (nanocrystalline) gas mixtures and deposited on common tungsten carbide tools. High resolution surface electron microscopy, Raman spectroscopy, friction, wear and scratching resistance tests were performed to study properties of the four series of DC. It was shown that such multilayer DC not only display good adhesion and wear resistant properties, but also have high surface smoothness and extremely low friction coefficient.

**Keywords**—diamond coatings; cutting tools; microwave CVD deposition; nanomaterial engineering; composite materials; SEM; Raman spectra; friction; machining forces; failure mechanism

### I. INTRODUCTION

Modern composite materials in addition to high specific strength, stiffness, and heat stability, demonstrate record-breaking abrasive ability, which significantly reduces the cutting tool life when machining and the possibility of wide application in industry. An important class of materials is given by Al-SiC metal matrix composites and carbon fiber plastics consisting of a matrix reinforced by fine particles and threads of carbon, glass, or light metals. Machining these materials by a carbide tool with reinforcing coatings based on oxides, nitrides, borides, and carbides of Al and Ti ( $\text{TiC}$ ,  $\text{TiB}_2$ ,  $\text{TiN}$ , and  $\text{Al}_2\text{O}_3$ ) often cause internal damages [1], which are attributed to considerable cutting forces that lead to breaks of fibers, exfoliation, fissures, and even melting as a result of overheating. To reduce the cutting forces, one needs a superhard cutting tool with sharp edge, low roughness, and very high abrasion resistance.

The fabrication of such a tool is based on the use of the unique properties of a polycrystalline diamond coating (DC) deposited from a gas phase on a hard-alloy substrate (CVD - chemical vapor deposition). CVD diamond coatings are

much superior to other in view of their extremely high hardness, record low friction coefficient, chemical stability, and high heat conductivity [2-4]. The combination of these qualities provides machining with much lower cutting forces, which is the main reserve for increasing the cutting speed, improving the quality, and extending the durability of the tool. In [5], the authors show that a WC-Co substrate with DC demonstrate an order of magnitude higher wear resistance than bare WC-Co substrates without coating in the tests carried out on silumin alloys. Moreover, the work surface after machining with tool covered by DC has reduced roughness compared with a surface after bare WC-Co tool and a WC-Co tool coated with titanium nitride [6]. Thus, a DC not only extends the tool life but also ensures a better quality of the material processed

One of key problems in the development of technologies for that fabrication of tools with DC is the increase of the adhesion of the coatings [7-8]. Under high thermal stress during CVD deposition of diamond in the presence of a cobalt binder, which catalyzes the formation of a graphite phase at the diamond-alloy interface, one can observe a partial or complete loss of adhesion between the coating and the substrate. The problem of adhesion is a topical problem, just as it has been two decades ago [9-10], because a universal technique for its solution has not yet been developed.

An additional increase of the adhesion with the substrate and the improvement of cutting properties of a tool can be achieved by forming bi- and multilayer DCs. There have been a few publications on the deposition and properties of bi- and multilayer micro/nanocrystalline composite DCs [11-12] in which a nanocrystalline diamond layer is deposited as upper layer. In this configuration of coatings, one can ensure high stiffness and good adhesion of microcrystalline DCs [11] together with low roughness and high elasticity of nanocrystalline DCs [13]. The application of multilayer DCs allows one to prevent cracking [14] and increase heat conductivity [15].

The goal of the present study is to work out a technology for producing for industrial applications highly resistive multilayer nano- and microcrystalline CVD DCs with improved adhesion in microwave plasma with indirect heating on WC-Co substrates, as well as the analysis of their structure and mechanical properties.

## II. DEPOSITION OF DIAMOND COATINGS

### A. Preliminary Processing to Block Cobalt

As substrates, we used multifaceted 12.5x12.5x3.5-mm cutting plates of WC-Co (6%) with a rear angle of 11 degrees (GOST 19064-80) produced by KZTS.

One of fundamental problems in depositing DCs on the substrates of WC-Co hard alloy is the catalytic action of cobalt in the alloy, which gives rise to  $sp^2$ -carbon instead of diamond when depositing the latter from a gas phase; cobalt may exist both on the growth surface of the DC and in the gas phase. Thus, one should carefully avoid the conditions of the pro

To remove cobalt from the surface of hard-alloy plates and minimize its effect on the processes of nucleation and deposition of DCs, we applied a method of stage-by-stage processing of the substrate, first, at the level of subgrains of tungsten carbide, and then on a cobalt binder located at the boundaries of micrograins. At the first stage, we used Murakami's reagent, which represents an aqueous solution  $K_3[Fe(CN)_6] : KOH : H_2O$  in proportion of 1 : 1 : 10, and, at the second stage, we etched with Caro's acid in the form of a solution of sulfuric acid in hydrogen peroxide water solution [4, 16]. Murakami's reagent acts on carbide grains, making the surface of the substrate rough, while Caro's acid oxidizes the binder to a soluble compound, thus reducing the surface concentration of cobalt.

### B. Deposition of a Barrier Layer

To improve the adhesion and eliminate the mobility of the binder, as well as possible clustering of cobalt at the stage of nucleation of diamond, we developed a technology of deposition of tungsten (W) barrier layers, which consists of two stages: (1) ion beam activated deposition of a thin (10÷30 nm) tungsten sublayer on a substrate at operating pressures of magnetron discharge less than 0.25 Pa followed by (2) the film growth at optimal pressures of 0.5÷0.7 Pa. This technology provides a moderate growth of accumulation of internal stresses and maintains the continuity of the film up to a thickness of 1200 nm. Before deposition, the substrates were cleaned by an ion beam for 5 to 120 minutes. The hardness after deposition of layer W compared with the etched surface increased by 2.5 units and amounted to  $HRC = 77.1$ . The Vickers microhardness (ISO 14577-1:2002) for maximum indentation depth of  $h_{max} = 0.59 \mu m$  and a loading speed of  $V = 13.3 mN/s$  was  $Hv_{100} = 1600$ . The ratio of the initial elastic deformation to the total mechanical work of indentation reduced to 37 %. By the results of the tests for adhesion, microhardness, and the friction coefficient for single-layer DCs [17], we established that the optimal thickness of the W layer is 600 nm. The adhesion of the deposited W coatings evaluated by scratch-

testing shows that continuous peeling occurs at a critical load of about 25 N.

### C. DC Deposition in Microwave Plasma

Diamond films were synthesized in microwave plasma in an ARDIS-100 (2.45 GHz, 5 kW) microwave plasma chemical vapor deposition reactor (<http://www.cvd-diamond.ru/>) with alternated supply of the  $CH_4/H_2$  and  $CH_4/H_2/N_2$  gas mixture at different stages of growth. The deposition of CVD-diamond was carried out for a total gas flow of 500 standard  $cm^3/min$  (sccm) and pressure of 65 Torr in the chamber under microwave power of 3.0 kW. The concentration of methane in the gas flow was 4% in all samples. Multilayer coatings represent sequences of layers of micro- and nanocrystalline DCs. Microcrystalline diamond (MCD) films were synthesized without addition of nitrogen, whereas, when synthesizing nanocrystalline diamond (NCD) films, the concentration of  $N_2$  in the total gas flow was maintained at a level of 4%. Temperature was measured through plasma by a Mikron M770 two-beam pyrometer and, looking at the substrates from one side and beside the plasma, by a Williamson 81-35-C two-color pyrometer through a gap in the wall of the substrate-holder. The substrate temperature during synthesis was 750°C and was kept constant. The deposition time in each series was about 5 hours. The deposition rate of DCs was 40÷50 nm/min.

In all the series, the first (lower) layer was a MCD film in view of its better adhesion to the substrate [18]. We carried out 4 series of experiments in the following order of growth time of layers:

1 series: MCD (75 min) + NCD (75 min) + MCD (75 min) + NCD (75 min);

2 series: MCD (120 min) + NCD (90 min) + MCD (60 min) + NCD (30 min);

3 series: MCD (30 min) + NCD (60 min) + MCD (90 min) + NCD (120 min);

4 series: MCD (150 min) + NCD (150 min).

## III. EXPERIMENTAL

To analyze the structure, composition, and local stresses in deposited DCs, we used Raman light scattering (RS) and photoluminescence (PL) (LabRAM HR 800, Horiba, spectrometer with excitation wavelength of 473 nm). The surface morphology and the phase of DCs were analyzed on a JSM-7001F scanning electron microscope with an INCA Energy 350 XT energy dispersive spectrometer and an EBSD of type HKL Channel 5 system for the analysis of the phase composition, structure, and texture of crystalline materials. The geometry and the profiles of the surfaces of DCs were measured on a New-View 5000 (Zygo) optical profilometer.

### A. SEM

The top-view SEM image of MCD/NCD coatings is typical to the nanocrystalline diamond films (Fig. 1).

The nitrogen addition affects the morphology of synthesized diamond crystallites [18]. The cauliflower-like clusters made by fine grains are found in the large scale SEM image of NCD film (Fig. 1). The high-resolution SEM

micrograph further evidences the nanocrystalline nature of NCD film consisting of fine grains smaller than 100 nm. It is interesting to note that large clusters (smaller than 200 nm) composed of fine grains show square-like or triangle-like sharp edges, in a manner similar to large {100} or {111} facets found usually in MCD. The RMS roughness of the growth surface of MCD/NCD coatings are 500 nm over  $178 \times 133 \mu\text{m}$  measured by optical profiler Zygo.

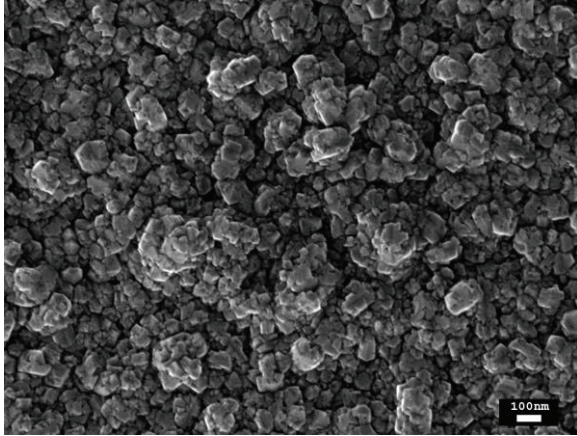


Figure 1. Surface morphology of multilayer #3 MCD/NCD film deposited on WC-Co plate.

### B. Raman Spectra

To study the profile of multilayer DCs, we applied confocal Raman spectroscopy. Samples for Raman spectra measuring were separated from WC-Co substrate as a result of the Rockwell adhesion test of DCs.

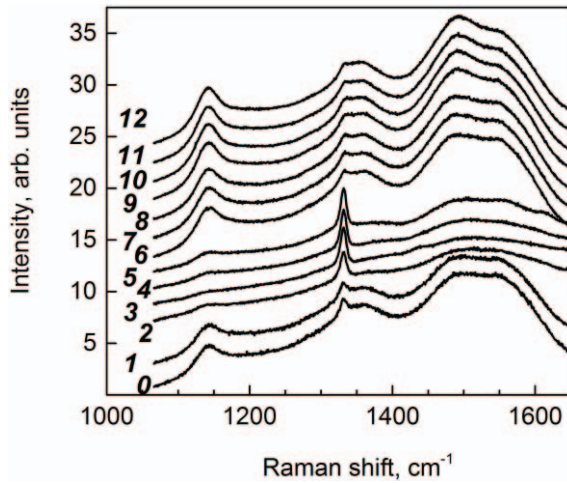


Figure 2. Transformation of the Raman spectrum of a bilayer #4 MCD/NCD coating. Numbers at the spectra correspond to the distance in microns from the nucleation side of the DC. For clarity, the spectra are shifted along the vertical.

The size of a laser spot while scanning was  $1 \mu\text{m}$ , and the scanning step was  $0.5 \mu\text{m}$ . Fig. 2 demonstrates the transformation of Raman spectra along the thickness of structure #4. All the spectra contain five bands of variable intensity. The maximum of the diamond peak in the Raman

spectrum (with a FWHM from 10 to  $20 \text{ cm}^{-1}$  (Fig. 3)) is at  $1332\text{-}1333 \text{ cm}^{-1}$ . In the measurements of DCs on substrates, this peak is shifted from the normal position at  $1332.5 \text{ cm}^{-1}$  to  $1336\text{-}1337 \text{ cm}^{-1}$ . These shifts correspond to compressive strength of 2.0-2.5 GPa due to the difference in the thermal expansion coefficients of the DC and the substrate. These values of stresses are regarded as optimal when depositing a DC on WC-Co. Usually they are between 2 and 5 GPa. In addition to the diamond peak, the Raman spectrum (Fig. 2) contains D ( $1360 \text{ cm}^{-1}$ ) and G ( $1554 \text{ cm}^{-1}$ ) bands due to disordered nondiamond  $\text{sp}^2$ -carbon and band characteristic of nanocrystalline DCs at  $1142$  and  $1490 \text{ cm}^{-1}$ , attributed to the  $\nu_1$  (in-plane CH bending combined with CC stretching) and  $\nu_3$  (C=C stretching) vibration modes, respectively, of trans-polyacetylene (TPA) hydrocarbon chains on intercrystallite boundaries. The relation between the intensities of bands varies along the thickness of the film. According to the Raman spectroscopy data, microcrystalline DC starts to form at a film thickness of  $1\text{-}1.5 \mu\text{m}$  (Fig. 3), which does not adversely affect the good adhesion, high hardness (85 in HRC units), and wear resistance of a bilayer DC. The transition region from micro- to nanocrystalline DC is well determined by the broadening and decrease of the relative intensity of the diamond band in the Raman spectra (Figs. 2 and 3). The deposition rate of NCD was  $50 \text{ nm/min}$ , and that of MCD,  $30 \text{ nm/min}$ .

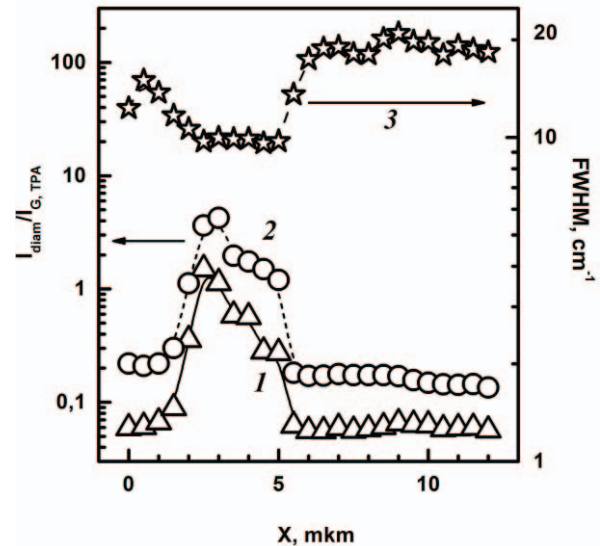


Figure 3. Variation of the intensity ratio of the diamond band to TPA and G- ((triangles-1 and circles-2, respectively) bands, and the FWHM of the diamond peak (asterisks-3) while measuring the Raman spectra across a chip in a  $12\text{-}\mu\text{m}$ -thick bilayer #4 MCD/NCD coating; X means height, zero corresponds to the nucleation side of the MCD/NCD coating.

When passing from the growth modes of microcrystalline to nanocrystalline DCs, it is important to prevent the formation of a layer with high concentration of  $\text{sp}^2$ -carbon on their interface [14, 19] and simultaneously ensure the formation of a smooth and strong DC. Judging by the Raman spectroscopy data, after the addition of nitrogen to MW CVD reactor a  $2\text{-}\mu\text{m}$ -thick transition layer is formed (Fig. 3), which combines the properties of micro- and nanocrystalline



DCs and, according to the data of [14, 19], increases the resistance of DCs on WC-Co plates to extreme mechanical and thermal loads.

### C. Tribology

Friction and wear characterizations were carried out by the sliding method on a “Tribometr” of CSM Instruments (Switzerland) by the «ball-on-disk» scheme under reciprocating motion of a rider along a 4-mm path. As the rider, we used a  $\text{Si}_3\text{N}_4$  ball. The structure of wear striations on the disk and the size of wear scars on the balls were studied by an AXOVERT CA25 (Carl Zeiss) optical microscope, and the profile of wear striations was measured on a SURFTEST SJ-402 (Mitutoyo) optical profilometer.

The difference in the structure and morphology of multilayer DCs of hard-alloy cutters manifest themselves in the study of their tribological properties. One can distinguish three different regimes of friction in the time-dependence of the friction coefficient of the samples. In the first initial region (of about 10 cycles or a path of less than 1 m), the friction coefficient rapidly grows to a maximum value in the second region ( $0.4\div 0.5$  for the DCs considered), and, only after 100-150 cycles (a path of  $\sim 10$  m) after achieving the regular friction mode decreases to about 0.045 for structures #2, #3, and #4 and to 0.16 for structure #1 with the least developed surface. The rapid decrease in the coefficient observed in tribological tests is characteristic of samples with high hardness, while low friction coefficients are characteristic of smooth nanocrystalline DCs. A short-time initial peak is attributed to both the blocking effect on the boundary between a  $\text{Si}_3\text{N}_4$  ball and sharp tips of irregularities on the DC surface in the beginning of testing and variation in the state of the DC surface during the tests.

The durability of DCs under tribological tests was estimated by the results of fractographic analysis of a wear striation on a sample and a wear scar on the rider (a ball). We could not form wear striations on the structures tested under a load of 1 N; the reduced wear of structures #1-#4 did not exceed  $10^{-8}$   $\text{mm}^3/\text{N}\cdot\text{m}$ . The reduced wear of the ball material ranged from 1.0 to  $1.4\times 10^{-4}$   $\text{mm}^3/\text{N}\cdot\text{m}$ , while the maximum wear was observed while testing structure #1, for which the friction coefficient was maximal. Moreover, the Raman spectra measured in the domain where the tests were carried out did not exhibit variations compared with the neighboring regions of DCs.

### D. Dry Machining Performance

To assess the wear resistance of cutters, we applied a method of dynamometric measurements, which allows one by controlling the cutting forces to maintain constant pressure on friction surfaces of tooling and structural materials in a wide range of speeds during tests. Durability tests while machining A390 silumin were performed on bare, MW diamond coated WC-Co plates and CVD commercial hot filament DCs of Sandvik (<http://www.sandvik.coromant.com/en-us>). Test mode for all samples had the same conditions: mean cutting speed of 200 m/min, length feed of 0.15 mm/rev., and cutting depth of 0.5

mm. Wear resistance was determined by the length of the cutting path of the corresponding critical flank wear - 0.5 mm. The cutting path length to the critical wear was 2200 m for a WC-Co plate without coating, 9250 m with a single-layer MCD coating, 12300 m with #3 MCD/NCD coating, and 11500 m for a plate with Sandvik coating. The abrasion resistance indices well correlated with the friction coefficients on the front surface of the cutting plate.

### E. Scratching Resistance Tests

The adhesion / cohesion strength coatings research was conducted by measuring the scratch by Rockwell conical diamond indenter under a continuously increasing load on “Revetest” instrument (CSM Instruments, Switzerland). We examined the process of coating failure in the course of scratching by monitoring of the several parameters: loading force, acoustic emission intensity of the friction force and the depth of the scratch during displacement of the indenter. The analysis of the curves shape and an optical microscope observations of the destruction traces were used to determine the minimum allowed load  $L_c$ , leading to the DC destruction [20]. We have established that, for the multilayer #2 MCD/NCD coating, a local chip is caused by compressive stresses before the moving indenter, and complete abrasion/spallation of the substrate was observed at a load of 83 N. In the sample #3 MCD/NCD coating, failure occurs under slow abrasion of the coating with the formation of wear products and without local chips, and complete abrasion of the substrate was observed at a load of 63 N. Tests on a commercial reference sample of Sandvik have shown that a local cohesive chip on this sample within the coating thickness is caused by tensile stresses behind the indenter, and complete abrasion/spallation of the substrate was observed at a load of 26 N.

## IV. CONCLUSION

Multilayer diamond films are deposited from a mixture of methane, hydrogen and nitrogen as the reactant gases by the MW CVD method with indirect heating on WC-Co plates. To improve the interfacial adhesion, to limit the graphitization and to relax the residual thermal stresses a tungsten interlayer with a low diffusion coefficient for carbon and cobalt was used. Confocal Raman spectroscopy was used to study the profile of MCD/NCD coatings. It was shown that nitrogen doping of NCD increases friction, wear and scratching resistance properties of coatings in comparison with commercial hot filament DCs. This work provided new insights about optimizing the MW CVD of DC on WC-Co plates to produce adherent diamond coatings in the dry cutting manufacturing chain of high silicon aluminum alloys and carbon fiber plastics.

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