ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Formation of CDV-Diamond Film on the Agglomerated Particles of Stabilized Ceramic Nanopowder.

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ABSTRACT

The work analyzed formation process of diamond films produced by chemical vapor deposition method. Three stage chemical treatment of substrate from hard alloy was done to remove cobalt bundle from the surface, to prevent diamond-graphite junction on the stage of nucleation and promoted long-term maintenance of the process of diamond film growth. It was shown that the formation of diamond film is happened mainly on the agglomerated particles of ceramic nanopowder. Stages of diamond film formation on stabilized ceramic precursor were defined: formation and agglomeration of globules, roughening of globules structure and their coating with numerous faces {100}, geometrical selection, formation of secondary conic textures <110> and <111> and renucleation. In all spectra there is a peak in the region 1334.5 cm-1, connected with monocrystalline diamond, which is the evidence of film diamond phase.

Keywords: CDV-diamond film, ceramic nanopowder, the evolution of structure, phase composition.

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ISSN: 0975-8585

INTRODUCTION

Diamond films impart to the surface of hardened instrument or detail the ability to withstand high thermal and force loads arising at "dry" treatment of tough materials without restructuring and internal stress growth in friction zone. Due to this diamond films are used efficiently in different spheres of application: electronics, engineering, cutting tool industry and medicine.

Diamond films deposition has become available due to the development of chemical vapor deposition (CVD) method which gave the green light to the synthesis of diamond at low pressure far beyond the limits of its thermodynamic stability [1]. Production of CVD –diamond film with high adhesion to non-diamond substrate with Co in its composition is a very difficult problem as far as Co is the catalyst of diamond-graphite interface (junction, transition) which opposes continuous maintenance of the process of diamond film growth because of graphite sediment accumulation [2].

An application of nanocrystalline diamond films in medicine opens new intellectual horizons for a contemporary human, and allows for an enrichment of the present knowledge, technology and thought with elements, which are not completely understood but which in a significant way contribute to the development of technical applications in medical science [3].

In order to prevent graphitization of carbonic atoms, to substitute heterogeneous mechanism of diamond film growth to homogeneous one and to increase its adhesion strength it is preliminary carried out chemical treatment of non diamond substrate and is coated suspensions with inoculating micro particles of diamond. Additional introduction of Zr, Fe, Ti, Cu, Al_2O_3 powders into diamond suspensions promotes the intensification of diamond phase nucleation while the combination of powder large and small particles allows increasing the nucleation density by an order, excluding hollow space and, in the end, diminishing roughness and obtaining very thin uniform diamond films [4].

Influence of metal powders on the process of diamond films formation on non diamond substrates has been sufficiently studied [5-7]. Influence of oxide materials on parameters of nucleation and growth of diamond films is restricted. In this article it will be examined the influence of ZrO_2 ceramic nanopowder, stabilized by Y_2O_3-CeO_2, on nucleation and stages of diamond film formation on hard alloys.

EXPERIMENT

Before deposition of diamond film the surface of test samples from hard alloy VK6 (94% tungsten carbide and 6% cobalt) was treated mechanically and chemically.

To examine the microstructure samples of Ø 10 mm were mechanically polished by abrasive disks (P320, P800, P1200, P2000) of LaboPol-2 (Struers) grinding machines with the use of water and DP-Lubricant, and then they were polished with DP-Lubricant Blue polishing diamond liquid of 3 µm, 1 µm, 0.25 µm dispersion and diamond liquid, including Al_2O_3, of 0.1 µm dispersion by LaboPol-5 (Struers) polishing machine.

In order to etch cobalt bundle there was carried out three staged chemical treatment of test samples' surface in solutions of H_2SO_4, H_2SO_4:H_2O_2 (1:3), H_2O_2 during 10, 40, and 20 minutes, respectively. These etching agents were used for the reason of selective chemical etching of the surface. Time of action was chosen experimentally.

Ceramic powder of ZrO_2 with Y_2O_3 (2.2 mole %) and CeO_2 (3 mole %) addition agents, synthesized according to [8] technique was used as precursor of diamond. Besides ZrO_2-Y_2O_3-CeO_2 ceramic nanoparticles with the diameter of 65 nm agglomerate particles with average size of 10 µm were introduced in suspension based on isopropyl alcohol [9]. Preparation of suspension was realized in ultrasonic field of disperser «UZDN-2T» with operating frequency of 22 KHz during 30 min.

Treated surface of test samples was contained in glass boxes with suspension made on the base of stabilized ceramic powder. Boxes were placed in ultrasonic bath for 30 min. In order to remove the excess isopropyl alcohol test samples were dried by the stream of hot air just after ultrasonic treatment and then they were placed in the chamber of microwave CVD reactor AX 5200S-ECR (SEKI TECNOTRON).

ISSN: 0975-8585

Deposition of diamond film was carried out in CVD reactor at the following technological parameters: pressure of H_2:CH_4 gas mixture in the chamber of reactor was 25 Torr ($3.3 \cdot 10^4$ Pa), methane concentration in the total volume of gas mixture amounted to 1 %, temperature of samples' heating in the process of deposition was 700 ^{0}C, SHF power - 600 W. Time of diamond film deposition was increased from 1 to 4 hours for assignment of its forming stages. Phase composition of the received diamond film was studied by the procedure of Raman's spectroscopy at multifunctional spectrometer of Raman scattering "SENTERA" (Bruker) with the wavelength of laser emission of 532 nm. Microstructure and thickness of diamond films were examined by the procedures of scanning electron microscopy (SEM) at analytical field-emission scanning electron microscope ULTRA 55 (Carl Zeiss, German) with additional attachment for EDX-analysis.

RESULT AND DISCUSSIONS

Fig. 1 shows SEM picture of hard alloy surface after three-stage etching. Energy dispersive analysis of five points of the test sample surface didn't detect cobalt bundle along the boundaries of tungsten carbide grains (Fig.1, Table 1).

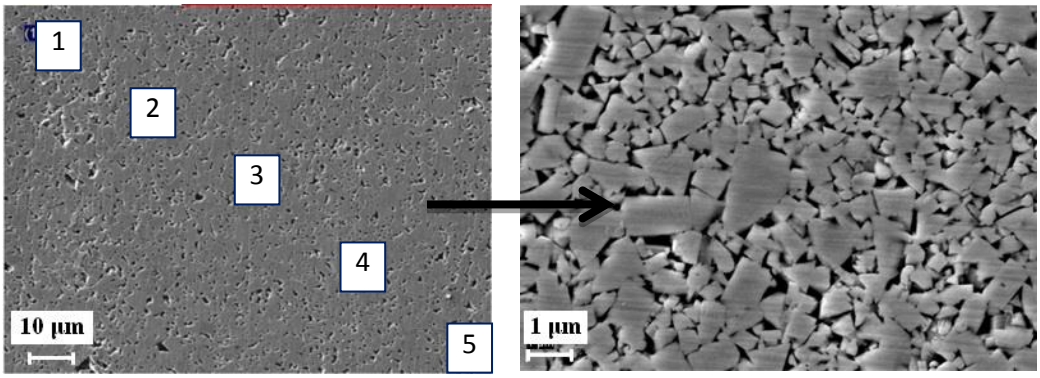

Figure 1: SEM image of the surface tungsten carbide of after a three-stage etching

Table 1: Elemental composition of test samples surface after etching

Element	Point 1, wt. %	Point 2, wt. %	Point 3, wt. %	Point 4, wt. %	Point 5, wt. %
C	6.13	5.8	5.36	6.44	6.36
W	93.87	94.2	94.64	93.56	93.64

Element-microscopic research of diamond films surface made possible to determine the stages of their formation.

I Globular stage – forming of the diamond in 3D formations with diameter up to 2.5 µm (Fig. 2). Forming of globules is happened mainly on the agglomerated particles of ceramic nanopowder (Fig. 3).

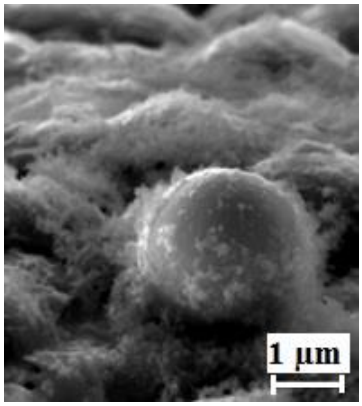

Figure 2: SEM image of diamond film on the globular stage

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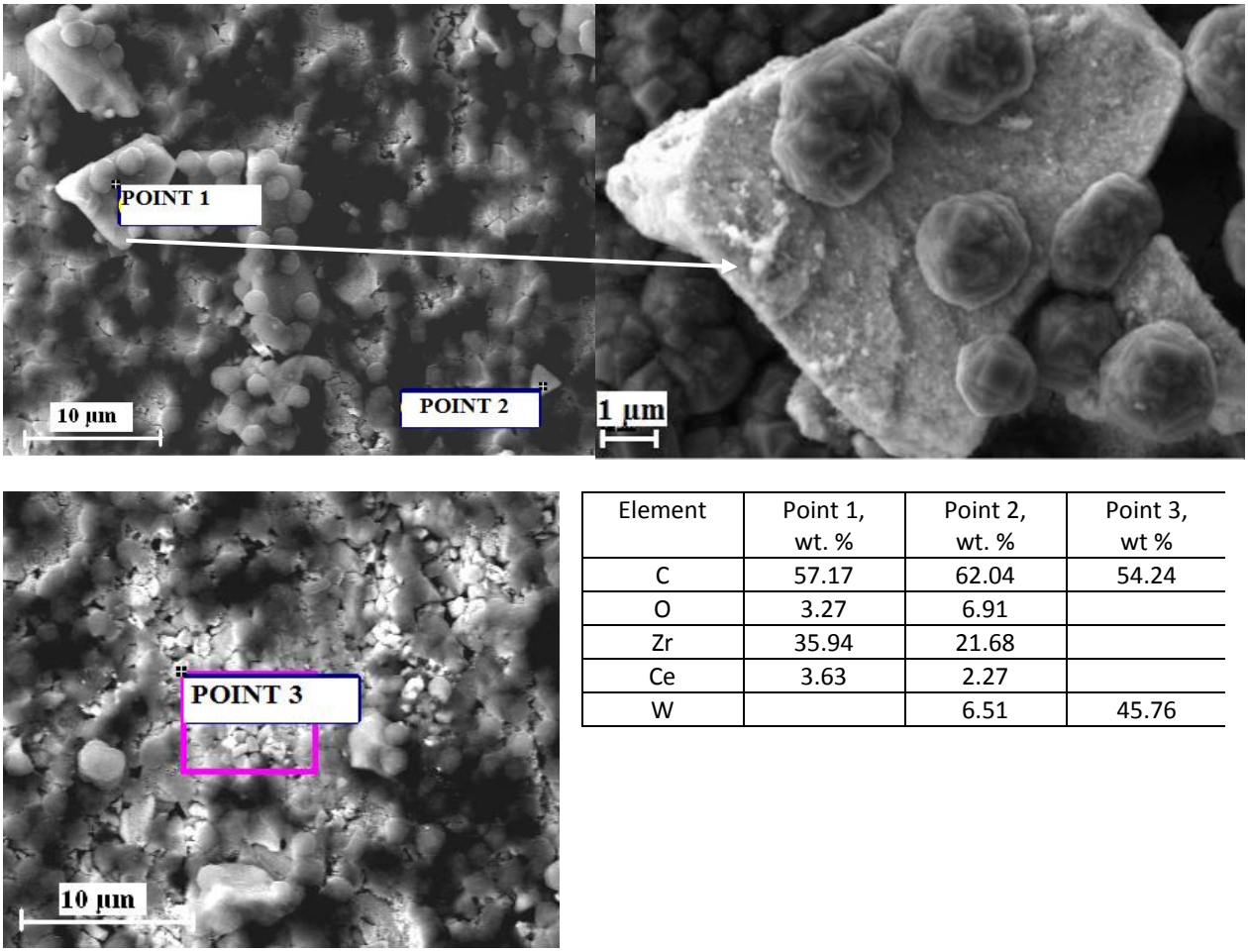

Element	Point 1, wt. %	Point 2, wt. %	Point 3, wt %
C	57.17	62.04	54.24
O	3.27	6.91	
Zr	35.94	21.68	
Ce	3.63	2.27	
W		6.51	45.76

Figure 3: EDX –analysis of tungsten carbide surface of diamond film on the globular stage

Few globules formed on the tungsten carbide grains (Fig. 4a) and in irregularities of substrate surface (Fig. 4b, left bottom corner) were found as well. Globules' diameter was in the range of 500 nm – 1 µm, thickness of irregular globular layer is in the range of 800 nm – 1 µm.

a) b)

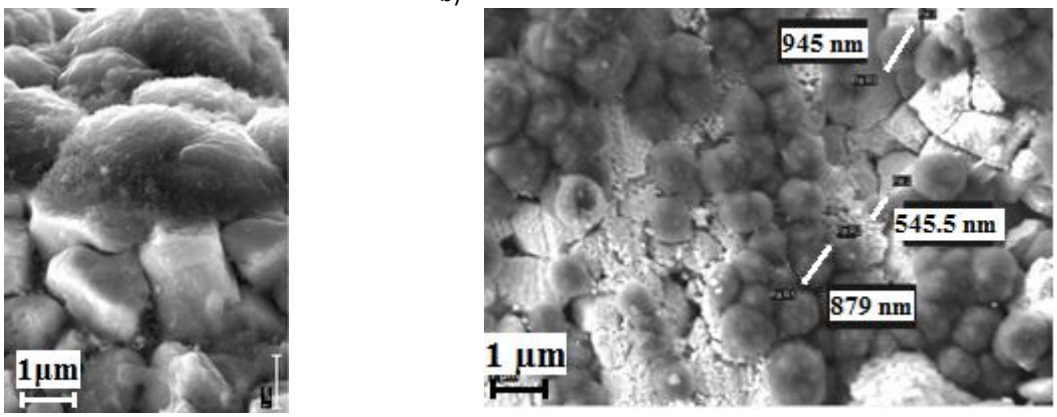

Figure 4: SEM images of diamond film on the stage of local formation of globules on the tungsten carbide grains (a) and in irregularities of substrate surface (b)

II *Stage of roughening of the globules structure and their coating with numerous edges {100}.* On the globular surface with the increase of globules' height it is formed the ramified system of incoming angles along the

boundaries of hemispheres promoting the rise of formation rate (Fig. 5). Appearance of faces {100} is the result of diamond layers' crystallization in conditions of partial or complete loss of morphological stability [10]. Cerium oxide being the component of ceramics composition begins to interact with carbon and acting as catalyst accelerates the process of diamond nuclei formation. The average thickness of the formed diamond layer amounts to 1.3 μm.

a) b)

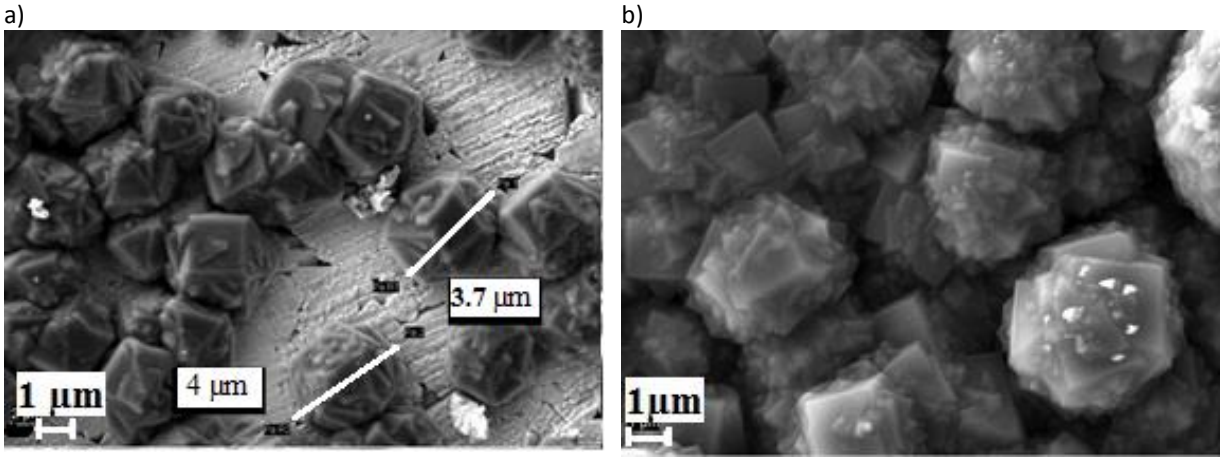

Figure 5 SEM images of diamond film on the stage of roughening of the globules structure (a) and their coating with numerous edges {100} (b)

On further staged of diamond film formation particles and agglomerates of ceramic powder were not detected. The results of EDX – analysis of diamond film surface - confirm this fact. It could be assumed that in plasma of atomic hydrogen it takes place the reaction of zirconium oxide reduction with formation of zirconium carbide or metal zirconium which is confirmed by the reactions presented below:

$$H_2 \rightarrow H+H$$
$$H+CH_4 \rightarrow C+H_2$$
$$ZrO2 + H + C \rightarrow Zr + H + CO + O$$
$$Zr+C \rightarrow ZrC$$

Thus, destabilization of ceramic powder structure can occur at its contact with atomic methane-hydrogen plasma.

III Stage of geometric selection. Formation of numerous small faces {100} on spherical surfaces inevitably results in Gross–Meller principle manifestation, namely in natural selection and further agglomeration of crystal grains the faces {100} of which are practically parallel to the substrate surface (Fig. 6). This stage leads to the appreciable texturing of crystal grains during the further stages of diamond film formation. The average thickness of the formed diamond film is 2.3-2.5 μm.

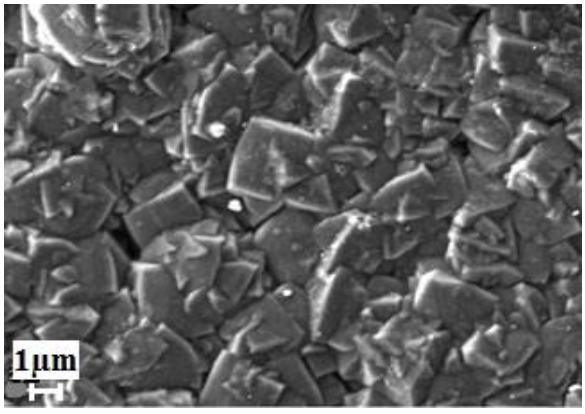

Figure 6: SEM images of diamond film on the stage of geometric selection

IV Stage of formation of secondary conic textures <110> and <111>. Formation of axial texture <100> is finished when diamond layer thickness achieves certain value determined by the conditions of deposition. High formation rate is supported by appearance of numerous reentrant angles at the expense of twinning on the plates' surface {100} (Fig. 7). Multiple twinning on every face {100} in accordance with spinel law explains formation of secondary conic texture <110> on axial texture <100>. Average thickness of the formed diamond layer is 2.3-2.5 μm.

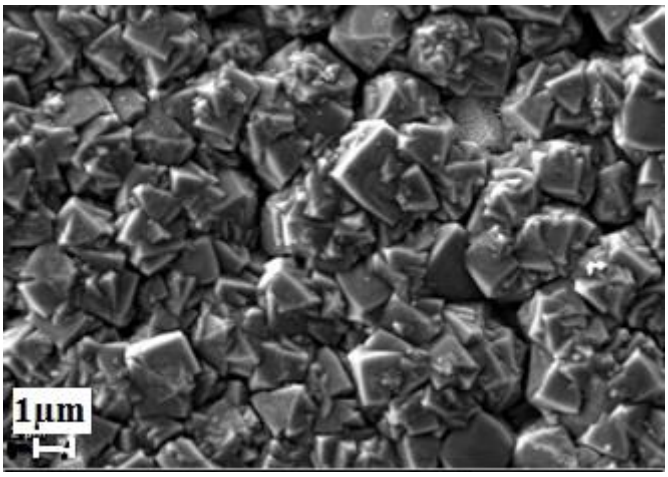

Figure 7 SEM images of diamond film on the stage of secondary formation of conic textures <110> and <111>

V Stage of renucleation.

Further process of diamond film formation is continued at the expense of renucleation (Fig. 8). Thickness of the formed on this stage diamond film is 3.3-3.6 μm.

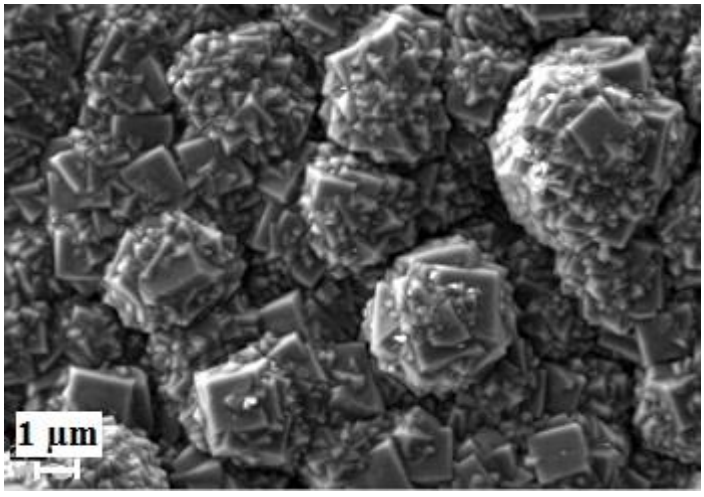

Figure 8: SEM images of diamond film on the stage of renucleation

Fig. 9 shows Raman spectrum (RS) of diamond films on test samples. For the ideal diamond lattice only one peak 1332.5 cm^{-1} with half-width not more than 5 cm^{-1} is identified in RS [11]. In all spectra peak in vicinity of 1334.5 $см^{-1}$ is presented (Fig. 9). It is connected with monocrystalline diamond which is the confirmation of diamond phase of the film [12]. Site shift in the direction of wave number increase is the specific factor for the diamond films which depends on the film structure and selected for the analysis laser emission. RS spectrum of diamond films there may be peaks both of diamond and non diamond component. Non diamond inclusions give characteristic properties in RS spectrum and line G is one of them – wide band with wave numbers of 1500-1550 cm^{-1}, appeared in case of amorphous sp^2-carbon [12-14]. Crystalline quality of diamond films is generally estimated by the correlation of integral intensity of diamond line (1334 cm^{-1}) and line G (1500 cm^{-1}): I_{1334}/I_{1500} [13, 14]. For example, if in spectrum wide peak in the region of 1500-1550 cm^{-1} is absent this

fact is the evidence of diamond film purity. With the synthesis time growth this correlation decreases as follows: 0.17; 0.12; 0.08; 0.04. This fact is the evidence of diamond phase rise and reduction of graphite impurities.

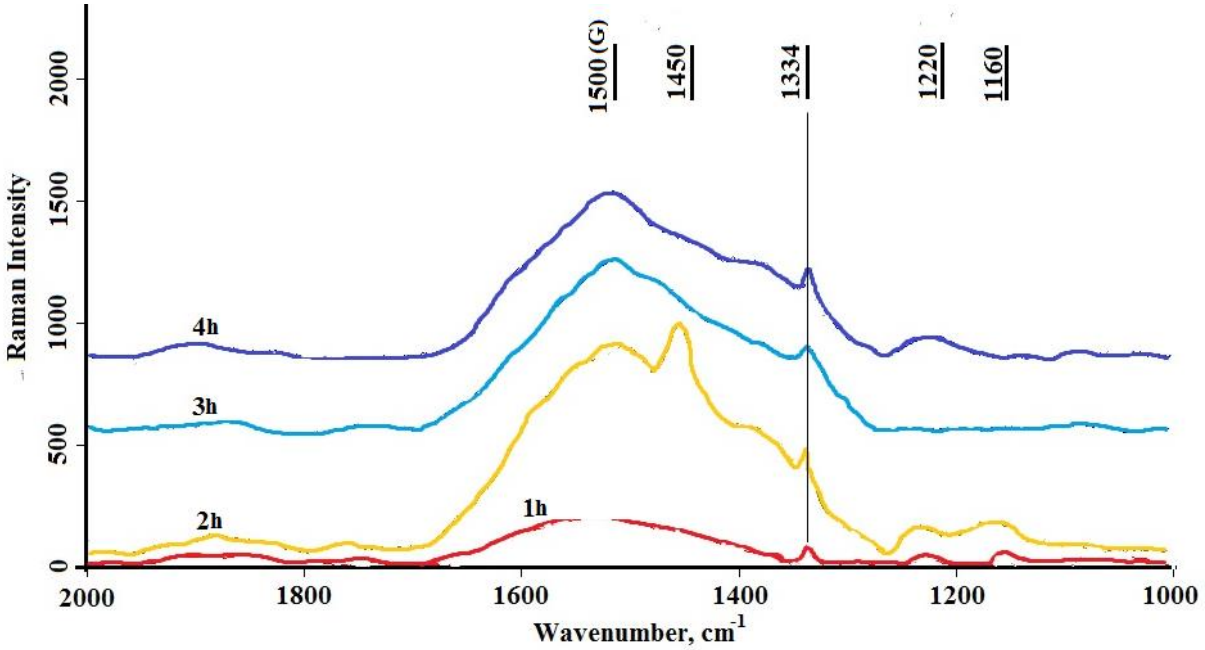

Figure 8: Raman spectroscopy of diamond film

Besides line G spectrum of nanocrystalline diamond films contains two additional lines in the region 1100-1250 cm^{-1} and 1430-1480 cm^{-1}, which are not connected with diamond sp^3-carbon phase but represent modes of trans-polyacetylene, segments formed on the intercrystalline boundaries of diamond grains [12].

Lines of trans-polyacetylene in spectrum of two hours synthesis grow by the intensity many times and identified well. This fact can be connected with diamond grain's size growth in the film as well as with dominant rise of faces in definite crystallographic direction which doesn't occur in less time of synthesis. In renucleation of diamond nuclei in the film (4 hours of synthesis) lines of trans-polyacetylene appear again which tells about formation of polymer phase on the boundaries of diamond nuclei.

SUMMARY

Three stage chemical treatment of substrate from hard alloy in solutions of H_2SO_4, H_2SO_4:H_2O_2 (1:3), H_2O_2 made possible to remove cobalt bundle from the surface, to prevent diamond-graphite junction on the stage of nucleation and promoted long-term maintenance of the process of diamond film growth.

Stabilized ceramic nanopowder contained in suspension composition promotes the rise of nucleation centers number and directed diamond film growth which is confirmed by formation of globular phase and its further roughening mainly on ceramic particle.

Stages of diamond film formation on stabilized ceramic precursor were defined: formation and agglomeration of globules, roughening of globules structure and their coating with numerous faces {100}, geometrical selection, formation of secondary conic textures <110> and <111> and renucleation.

In all spectra there is a peak in the region 1334.5 cm^{-1}, connected with monocrystalline diamond, which is the evidence of film diamond phase. Site shift in direction of wave number increase is the characteristic feature of diamond films which depends on film structure and selected laser emission. The longer is the synthesis the better is crystalline quality of the film. This fact is confirmed according to the reduction of integral correlation values I_{1334}/I_{1500}. Manifestation of trans-polyacetylene lines allows additionally identifying nucleation and growth of diamond grain.

Diamond layers are getting more and more significance in medicine, becoming a biomaterial of the highest, unmatched by other materials, degree of biocompatibility with the environment of human body.

ACKNOWLEDGMENTS

The research was financially supported by the Ministry of Education and Science of Russian Federation, research project №11.1913.2014/К – "Research of physico-chemical deposition processes of diamond films on ceramic materials"

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