Review: Diamond Metallization as a Method of Improving the Efficiency of Superhard Materials

L. P. Efimenko[a, b, *], S. P. Bogdanov[a], and M. M. Sychev[a, c]

[a]St. Petersburg State Institute of Technology (Technical University), St. Petersburg, 190013 Russia
[b]St. Petersburg Electrotechnical University LETI, St. Petersburg, 197376 Russia
[c]Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, 199034 Russia
*e-mail: efimenkolp37@mail.ru

Abstract—This article analyzes the current status of developments in the field of metallization of diamond powders as a method of improving the performance of cutting and drilling tools by increasing the level of diamond retention in the matrix of the superhard material. In recent years attention has been focused on the production of coatings based on carbide-forming metals (Cr, Ti, W, Mo, and others), providing a solid chemical bond of the matrix with the diamond surface. This article presents a physicochemical analysis of the published experimental data on the structure of the diamond–metal transition zone responsible for the level of diamond retention. The experimental results are demonstrated, which indicate a significant (in a number of cases over 50%) improvement in the efficiency of diamond tools upon use of metallized diamonds.

Superhard materials are an actively developed market segment for cutting and drilling tools. Diamond is characterized by unique physicochemical properties; among superhard materials it is characterized to have the highest hardness and wear resistance, the highest heat conductance, and the lowest coefficient of friction. During the operation of a cutting tool, the high level of heat conductance of diamond provides heat removal from the working area of cutting and, as a consequence, the production of items with an unburnt surface.

Diamond tools are widely used in various industries for cutting, grinding, drilling, and polishing hard materials, such as stone, concrete, cemented carbide, optical glass, ceramics, and other hard-to-machine materials and alloys. For instance, in the oil and gas industry, rocks are drilled by rotary bits equipped with Polycrystalline Diamond Cutter (PDC) cutters [1].

In order to improve the performance of cutting and drilling tools, various methods and approaches are being developed, including the use of diamond grains of varying dispersity, which ensures that the superhard particles are more densely packed. For instance [2], in order to increase the wear and corrosion resistance of drill bits intended for penetrating into deep oil wells, it is proposed to apply a protective coating containing both diamond microparticles (1–28 μm) and diamond nanoparticles (4–6 nm), uniformly distributed between the coarser microparticles in the following ratio: microparticles, 5.0–25.0 vol %; nanoparticles, 2.0–5.0 vol %; and the remainder, metal. The optimal thickness of a protective coating is 10–500 μm.

In superhard tools diamond is the basic working component; the function of the matrix is to retain diamond grains during operation; moreover, the wear rates of the matrix and diamond grains should be comparable.

Diamond composites are sintered at high pressures and temperatures, which results in their high cost; and industrially developed countries are carrying out projects devoted both to improving the existing, and developing new, more efficient production technologies for diamond tools.

The operating lifetime and performance of diamond tools are mainly determined by the diamond retention ability of the matrix. At present the studies devoted to improvement of performances of cutting diamond tools are being carried out in the following areas [3]. Pretreatment of the diamond surface: metallization or provision of the additional surface roughness of diamond particles; modification of the metal matrix by the addition of carbide-forming metals, rare earth elements, or nonmetallic elements (Si, P, and B); improvement of the compaction of composite diamond-containing material (sintering, hot pressing, etc.).

Upon modification of the matrix composition by the addition of carbide-forming metals, it is required to increase the temperature or time of the heat treatment for compaction of the composite material in order to provide a diffusive mass transfer of carbide-forming metals from the bulk of the matrix to the diamond surface and the reactive formation of binding carbide layer. The surface modification of powdered particles by the formation of functional layers on their surface, including the generation of core-shell nanoparticles, is an engineering approach that allows us to achieve the multifunctionality of the properties and significantly improve the performance of the new composite material [4].

The most promising way to improve the performance of superhard materials is the metallization of diamond grains, that is, the formation of coatings on the diamond's surface, providing a strong bond of the diamond with the matrix of the superhard material. The metallized diamonds are produced by advanced physical and chemical vapor deposition (PVD, CVD), galvanic methods, magnetron sputtering, deposition in molten salts, etc. New methods and approaches used for the production of functional coatings on diamond are being actively developed.

In Russia the methods of diamond metallization is developed in numerous R&D centers, including Larionov Institute of the Physical-Technical Problems of the North, Siberian Branch of Russian Academy of Sciences, Yakutsk; Ammosov North-Eastern Federal University, Yakutsk; Volgograd State Technical University; St. Petersburg State Institute of Technology; Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk; Novosibirsk State University; Moscow State University of Science and Technology; Berbekov Kabardino-Balkarian State University, Nalchik; Ivanovo State University of Chemistry and Technology; NIIgrafit, Moscow; and others.

In recent years the most active studies devoted to improving the performance of diamond tools have been carried out in China; the main area of investigations is the metallization of diamonds.

This review focuses on recent developments in Russia and abroad devoted to improving the performance of superhard material by the preliminary metallization of diamond as the most promising method of improving diamond retention: the main parameter determining the long-term efficiency of cutting and drilling tools.

DIAMOND METALLIZATION BY CARBIDE-FORMING METALS

Researchers are currently focused on the production of coatings based on carbide-forming metals pro-

viding a strong chemical bond of the matrix with the diamond surface, and hence, significantly improving the performance of the superhard material.

An integrated engineering approach was developed in [5−8] to produce diamond-containing composite materials, where one operation cycle of a vacuum furnace combines the thermal diffusive metallization of diamond by chromium, and sintering of the matrix based on hard-melting a powdered composition with simultaneous copper infiltration.

The possibility of producing diamond composite materials—Cr coating and WC−Co−Cu matrix—in the frames of a one-stage furnace heating−cooling cycle was demonstrated [5]. Natural diamonds with the dispersity of 315/250 and 250/200 were used. Each diamond grain was wrapped in a shell of finely dispersed powdered Cr with the thickness less than 1 mm. Preliminary heat treatment was carried out at 600°C for 30−45 min, and the composite material was formed on heating at 1100°C for 5 min. Carbides Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$ in the diamond−matrix transient layer with the thickness of 6 to 9 μm were detected by the physicochemical analysis. Comparative tests of the experimental samples demonstrated the efficiency of the metallization of diamond grains as a method of improving their diamond retention ability and, consequently, the performance of diamond tools. The specific efficiency of samples with metallized diamonds is 39% higher than that of materials based on diamonds without metallization.

The article [8] discussed the influence of diamond metallization on the specific efficiency of dressers with the WC−Co−Cu matrix based on hard-melting a powdered mixture, grade VK6, infiltrated with copper. Along the dresser's axis, five diamonds were placed with the average weight of 0.21 carat each (Fig. 1). Prior to placement into a hard-melting blend, the diamonds were wrapped in a thin copper foil, which was filled with powdered chromium in an amount equal to the diamonds' weight and uniformly distributed around the diamond grains.

Reference samples were prepared for the tests, based on nonmetallized diamonds, where the diamond retention was determined by the mechanical bond between the solidified copper infiltrate with micropores and the surface roughness of the diamond grains, formed as a consequence of the catalytic graphitization of diamond and its partial dissolution in the matrix.

It was established that, in the diamond−matrix's transient zone of the experimental samples, the thermal diffusive metallization by chromium resulted in the formation of a carbide layer with the thickness of ~5 μm, which closely adhered to the diamond grain with a composition similar to Cr_3C_2 (Fig. 2).
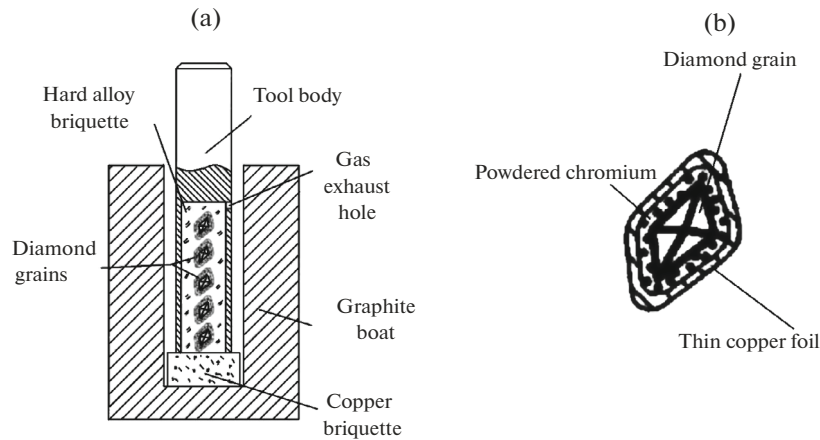
Fig. 1. Facility for dresser sintering by hybrid flowchart with self-dosing copper infiltration (a) and diamond grain wrapped in copper foil with powdered chromium (b) [8].
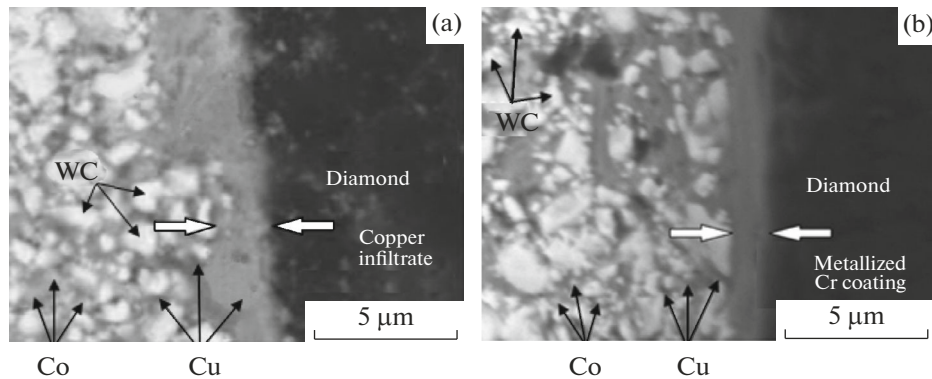

Fig. 2. Matrix structure near diamond−matrix transition zone of reference (a) and experimental (b) dressers [8].

Comparative tests of the reference and experimental dressers were performed to determine their specific efficiency upon the dressing of a grinding wheel made of green silicon carbide. The tests demonstrated the high level of efficiency of diamond metallization for composite instrumental materials. The specific efficiency of a diamond dresser based on the metallized diamonds increased by 44.7% in comparison with that of the reference diamond dresser produced by conventional sintering without metallization of the diamond grains.

A fundamental difference in the pattern of the diamonds breaking off from the matrix was detected upon during testing of the experimental and references dressers. In the reference samples, due to the low diamond retention of the matrix, caused only by the mechanical bond, whole diamond grains are broken off. In the experimental dressers, the diamond grains, firmly fixed in the matrix due to surface metallization, are broken off gradually, according to the mechanism of brittle transcrystalline chipping (minor flakes).

The diamond particles in [9] were metallized by thermal diffusion based on the sublimation of the metal in a vacuum with the subsequent deposition onto the surface of the diamond particles. Synthetic (AS2−AS6) and natural (A10, A25) diamonds were metallized. The coating based on a carbide-forming metal, chromium, was applied to the diamond grains; note that the sublimation temperature of this metal is relatively low: 992°C. Powdered diamond and chromium were mixed in various ratios and heated in a vacuum to temperatures above the metal sublimation threshold.

It was established that at the metallization point of 1100°C an intermediate porous layer formed on the diamond−coating interface, which weakened the mechanical properties of the structure. The authors provide two versions of the formation of the porous layer: a different rate of the diffusive mass transfer of the carbon and chromium atoms through the growing layer of the reaction products (carbides) and graphitization of the diamond surface in the presence of chro-
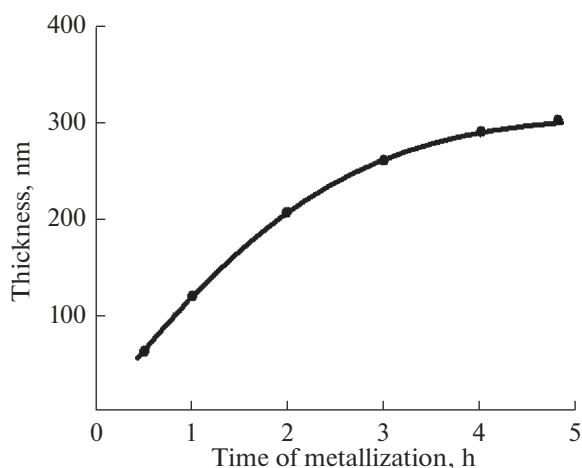
Fig. 3. Coating thickness on diamond, grade AS6 100/80, as a function of chromium metallization at 1000°C [9].

mium, which catalytically decreases the temperature of the transfer of diamond into graphite.

The optimal temperature was determined to be 1000°C, at which a dense coating with a metallic gloss was obtained on the diamond particles, which closely adhered to the substrate. The X-ray patterns show the diffraction maximums of Cr and Cr_7C_3, Cr_3C_2 carbides. It was established that the growth rate of the metallic coating depends on the temperature and time of the heat treatment, the ratio of the components in the initial reaction mix (diamond : chromium), and the dispersity of the reagents. The growth rate of the coating layer decelerates in time and after ~4 h of heat treatment it is ~300 nm (Fig. 3).

Tests to break up synthetic diamonds, of grades AS2–AS6, demonstrated that metallization by chromium increases the strength of the grains by 1.5–2 times due to the healing of the microcracks and surface defects of the diamond particles.

An advantage of the technology [9] is its relative engineering simplicity and possibility of multiple use of powdered chromium for the metallization of several batches of powdered diamonds. The project [9] was implemented at the plant of precious stones (Chelyabinsk oblast) and AO Volgograd Plant of Tractor Parts and Normals. Under the same experimental conditions, the metallized natural Splitter diamonds were reliably fixed in a holder and operated until they were completely worn out, whereas the diamonds without a metallic coating were used up to 60% and then dropped from the holder and were destroyed. The resistance of dressers based on metallized synthetic diamonds, grade AS15 25/200, was by 1.5–2 times higher than that of dressers 3908-0064 of state standard (GOST) 607 manufactured at AO Terek.

The possibility to apply iodine transport for diamond metallization in reactors without a temperature gradient was described in [10–12]. In most gas transport systems, a volatile compound is formed in one reactor zone and it is transferred to another reactor zone purposefully by the creation of a gradient of the temperature or pressure.

In the developed method of iodine transport [10–12], the directed gradient of temperature or pressure was not specially created. Metallization was carried out using carbide-forming metals (W, Ti, Cr), and the strong chemical interaction at the diamond−metal heterogeneous boundary provided the gradient of the chemical potential required for the transfer of iodides to the reactive surface of diamond. Volatile metal iodides are formed at 300−700°C.

A mixture of powdered diamond, metal (W, Ti, Cr), and iodine was loaded into a vacuumized quartz reactor. Powdered diamonds in a wide range from 1/0 to 500/400 μm were used. Based on the experiments, ceramic metal coatings on diamond were obtained. Table 1 summarizes the optimal temperatures for the production of coatings and their phase composition. It was established that with an increase in the temperature and time of the experiments, the content of the metal phase in the coating decreases with an increase in the carbide phase.

Films on the grains of detonation nanodiamond with a predicted thickness of 0.5 to 3 nm were obtained by the iodine transport of titanium. The metallized powdered nanodiamond was compacted at 4−5 GPa and 1300−1700°C. Superhard materials with an open porosity of less than 1% and total porosity of 3 to 10% were produced. The compressive strength of the samples was 6−12 GPa and the microhardness was 50−90 GPa, which is comparable with the microhardness of polycrystalline diamonds obtained at 7−14 GPa. It was impossible to obtain compact materials based on the powdered nanodiamonds without metallization at a pressure below 7 GPa.

Table 1. Properties of coatings on diamond produced by iodine transport in optimal modes [10−12]

Transported metal	Temperature, °C	Coating color	XRF results
Ti	500−800	Black	Diamond, TiC, Ti traces
W	1100	Grey	Diamond, WC, W_2C traces
Cr	500−800	Grey	Diamond, Cr, C_3C_2

The production of a WC coating on diamond in molten Na_2CO_3-NaCl salts at $630-680°C$ was described in [13]:

$$W + Na_2CO_3 \rightarrow 0.6WC \\ + 0.4Na_2WO_4 + 0.4Na_2CO_3 + 0.2Na_2O. \quad (3)$$
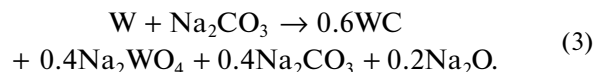
Synthetic powdered diamonds with the dispersity of 10 to 20 μm were used. The surface of tungsten particles was preliminarily oxidized at 400°C for 1 h. The ratio of molten salts $Na_2CO_3 : NaCl$ corresponded to the eutectic point (631.7°C), which allowed us to treat the diamonds and obtain a WC coating at the temperature below the melting points of Na_2CO_3 (856°C) and NaCl (800.7°C).

The production method of superhard diamond material for cutting and drilling tools was developed by the applying W–WC–F coatings on diamond grains [14]. The first adhesive layer formed directly on diamond contains powdered tungsten and tungsten carbide fused with fluorine. At the optimal content, fluorine increases tungsten's reactivity relative to carbon and tungsten's mechanical properties. It was established that the adhesive, mechanical, and protective properties are improved in a narrow range of the fluorine content: 0.001–0.12 wt %. A fluorine content below 0.001 wt % is insufficient to improve the tungsten's reactivity or the mechanical and protective properties of the coating. At the content above 0.12 wt % of fluorine, the risk of impairment of the coating's adhesion increases, especially when the tool operates at higher temperatures and in aggressive mediums. The developed coating is thermally stable up to above 800°C and it protects diamonds against oxidation and aggressive metals; moreover, the coating improves the retention of diamonds in cutting and drilling tools.

The possibility to apply microwave heating for the production of a titanium coating on diamond was demonstrated [15]. Synthetic diamonds with the average size of ~120 μm were used.

The coating was formed according to the following chemical reactions:

$$TiH_2(s) \rightarrow Ti(s) + H_2(g), \quad (1)$$

$$Ti(s) + C(s) = TiC(s). \quad (2)$$
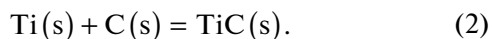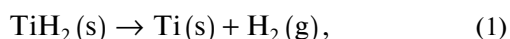
Heat treatment of the compositions was carried out in a microwave oven in an argon environment at 660–860°C for 1 h and the heating rate was ~80°C/min. The X-ray phase analysis after annealing revealed the phases of diamond, Ti, and TiC in the composition; moreover, with an increase in the annealing temperature, the intensity of the diffraction maximums of TiC increased. The optimal temperature for the formation of a dense coating was determined to be 760°C, at which its adherence to diamond was strongest. The layer thickness of coating was ~257 nm.

The growth kinetics of the TiC layer according to Eq. (2) is controlled by the rate of diffusion of the mass transfer of the Ti and C atoms across the TiC layer; moreover, the coefficient of diffusion of Ti in TiC (2.6×10^{-18} m^2/s) is significantly higher than that of carbon's diffusion in TiC (9.9×10^{-23} m^2/s) [15]. It was established that there exists an exterior layer of pure Ti on the surface of diamond particles, since the deposition rate of Ti by Eq. (1) is higher than the rate of its diffusive mass transfer in the TiC layer by Eq. (2).

The advantage of the microwave technology lies in its high heating rate and relatively low treatment time of the composition (~1 h), which allows decreasing the level of diamond graphitization [15].

The possibility to apply spark plasma sputtering for the production of a Ti coating on diamond was demonstrated [16]. Electric discharge treatment was applied to powdered mixtures containing diamond grains of 90 to 106 μm and powdered titanium. With the initial powdered composition in the range of 2.5 to 20 wt %, Ti two-phase coatings (TiC, Ti) were obtained, chemically bonded with the surface of the diamond grains. The metallization increased the ultimate compressive strength of the diamond grains by 15.7% (in comparison with the initial powdered diamonds).

Nanosized titanium/nichrome double-layer films were obtained in [17] on artificial polycrystalline diamonds, grade ASB-4, by ion plasma sputtering (vacuum: 10^{-2} Pa, 600°C). The X-ray phase analysis of the films after sputtering determined the following phases: Ni_4Ti_3, Cr_7Ni_3, Cr_2Ti, NiTi, Cr, and C. Additional treatment of diamond with the film at 1200°C for 4 min did not significantly modify the phase composition. The most intensive interaction takes place between the metal nanolayers of the Ti/(Ni, Cr) coating with the formation of intermetallic compounds. No titanium and chromium carbides were detected in [17], which could be attributed to the nanosized thickness of the internal carbide layer generated directly on diamond and the sufficiently ow sensitivity of the X-ray phase analysis.

The influence of a nanosized titanium/nickel double layer coating on specific efficiency of dressers based on polycrystalline synthetic diamonds, grade ARS-4, was studied in [18, 19]. It was demonstrated that, during the dressing of the grinding wheels, the Ti/Ni double layer coating increases the specific efficiency of the dressers by 40–55%. Diamonds without a coating lost efficiency after wear of 70–75% of their initial volume and dropped out of the matrix. Under the same experimental conditions, diamonds with a Ti/Ni double layer coating loss their efficiency only after wear of more than 90%.

Diamond–copper and diamond–aluminum composite materials with high heat conductance are now

Table 2. Bonding strength of diamond−metal contact pairs [29, 30]

Contact pair	Bonding strength, σ_{break}, MPa
Diamond−iron	24.12
Diamond−chromium	6.76
Diamond−cobalt	0.68
Diamond−titanium	−

being actively developed for electronics application [20−26]. The preliminary metallization of diamond particles is increasingly often used as a method for the higher cohesion of diamond grains with a matrix; moreover, the coatings are generally based on carbide-forming metals Cr, Mo, Ti, and W.

In [24] the WC coating on diamond particles was obtained on molten salts NaCl : KCl = 1 : 1 using powdered synthetic diamond, grade MBD8, with the particle size of ~70 μm and powdered oxide WO_3 with the particle size of ~45 μm. The diamond grains were treated in a salt bath at 900−1050°C for 1 h. The most uniform coating was obtained at 1050°C with the layer thickness of ~1 μm. The X-ray phase analysis of the coating detected the following phases: WC, as well as WO_3, W, and W_2C. Under similar compacting conditions, the use of metallized diamond particles made it possible to increase the density of the diamond−copper composite materials from 97.5 to 99.5%.

Metallization in [25, 26] was carried out by diffusion in the powdered compositions, and Ti and W coatings were obtained on diamonds. The optimal production mode of the W coating was determined: 900°C, 1 h [25]. Synthetic diamonds of ~400 μm were used and the thickness of coating layers was ~310 nm. The X-ray phase analysis of the composition after the thermal treatment determined the WC, W_2C, and W phases. The application of metallized diamonds made it possible to improve the thermal conductance of the diamond−copper composite materials produced by hot pressing [25, 26].

Using rotary chemical vapor deposition (RCVD), tungsten and nickel containing coatings were produced on the surface of synthetic diamonds [27]. Tungsten carbonyl $W(CO)_6$ and nickelocene $Ni(C_5H_5)_2$ were used as the gaseous precursors. Based on the metallized powders, heat conducting diamond−copper materials were obtained. The powders containing 50 vol % diamond with particles of 50, 100, and 200 μm were compacted by electric spark sintering and hot pressing. It was established that the highest relative density (97%) and heat conductance is found in the composites obtained by electric spark sintering based on diamonds of ~50 μm with a tungsten carbide coating.

Applied Diamond, Inc., United States [28], proposes various types of diamond metallization for high energy equipment. The standard flowchart of diamond metallization comprises three layers: a carbide-forming layer (Ti, W, Cr) having a strong chemical bond with diamond with the layer's thickness of ~100 nm; a diffusion barrier (Pd, Pt) to reduce the interaction between the chemically active internal sublayer and external functional layer with the layer's thickness of ~100 nm; and an external metal layer of the required composition with the layer's thickness of ~1 μm.

The experimental results simulating the conditions of the formation of intermediate layers at interaction of natural diamond with carbide-forming metals, Fe, Cr, Co, and Ti, at a high temperature were presented in [29, 30]. Natural diamonds were used for the production of contact pairs: diamonds with 17 faces, faceted and polished at the factory; the weight of the faceted diamonds was ~0.01 carat. The diamond crystals are transparent and slightly yellowish. The temperature and time sintering modes of the diamond−metal contact pairs corresponded to the operation mode of the vacuum furnace upon the production of hard-melting matrices of diamond containing tools with copper infiltration.

The shear strength of the obtained diamond−metal compounds was tested. The highest strength under similar experimental conditions was achieved for the diamond−iron contact pair (Table 2). It was concluded that minor additives of iron particles around the diamond grains can significantly increase the level of diamond retention of the ceramic metal matrices.

DIAMOND NICKELING

In recent years only a few works were devoted to diamond metallization by noncarbide-forming metals (mainly nickel), when the adhesion of the coating to diamond was determined by a mechanical bond.

The state diagram of Ni−C is a simple eutectic type of diagram, where the components are absent. Metastable carbide Ni_3C can be obtained only at the high cooling rates of the Ni−C melt or under higher pressures. During metallization there is no strong chemical interaction on the diamond−Ni heterogeneous boundary and strong adhesion of the coating to diamond can be achieved only on a rough diamond relief.

In [31] diamond nickeling was performed by the chemical reduction of the metal ions from solution. Synthetic diamonds of various dispersities were used, grades AS5 63/50, AS5S 100/80, and AS5 160/125. Prior to nickeling, the diamond powders were preliminarily treated in various etching solutions, without tin and palladium salts, aimed at increasing the relief's roughness and better adhesion of the nickel layer to the crystal's surface. Metallization of diamonds was car-
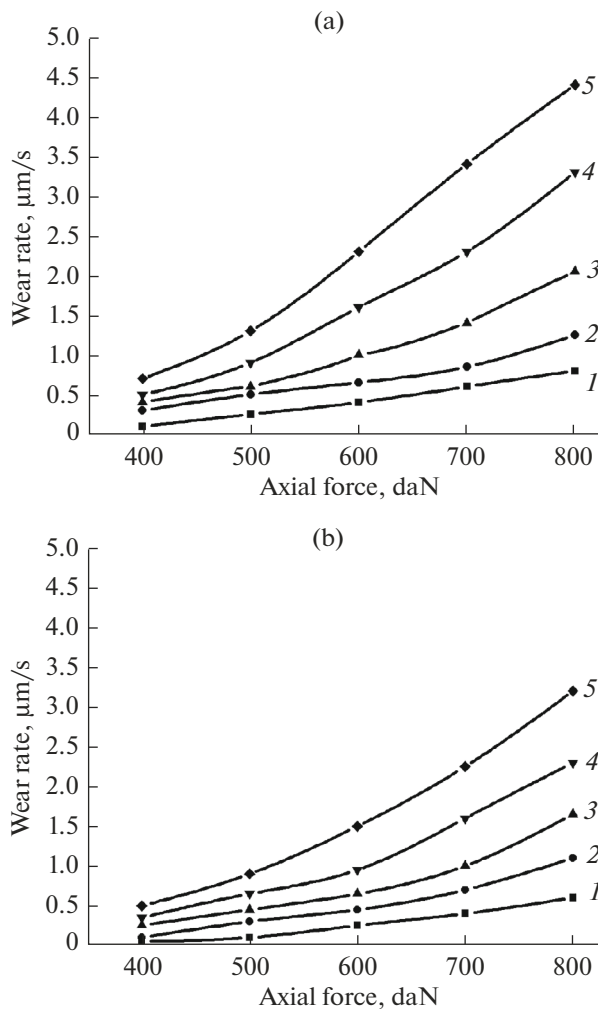
Fig. 4. Wear rate of drill bits equipped with nonmetallized (a) and metallized (b) diamonds as a function of axial force at various rpm: 600 (*1*), 750 (*2*), 950 (*3*), 1180 (*4*), 1500 (*5*) [32].

The experimental results aimed at improving the performance of drilling tools equipped with synthetic diamonds with various levels of metallization were presented in [32]. The efficiency of the drill bits significantly improves with the use of metallized diamonds.

Diamond nickeling exerted a positive effect on the mechanical rate of drilling and wear resistance of the drill bits developed at the Bakul Institute of Superhard Materials, Ukraine. Thee tests were performed with nickeled diamonds, grade AS125 250/200, with metallization levels of 25 and 50%. The thickness of the nickel layer was 3−5 μm. The drill bits were tested under commercial conditions upon drilling in the depth range of 50 to 1000 m.

It was established that the wear rate of the drill bits with metallized diamonds was 20−60% lower than that of the drill bits with nonmetallized diamonds (Fig. 4). When using nickeled diamonds that were 50% metallized, the average penetration per drill bit increased by a factor of 1.56; moreover, the specific consumption of the diamonds decreased by 37% (Table 3).

CONCLUSIONS

The efficiency of diamond tools is mainly determined by the diamond retention of the matrix of superhard material. New physicochemical methods and approaches to diamond metallization, aimed at improving the efficiency of diamond tools, are being intensively developed using a wide range of precursors; the temperature for the formation of coatings ranges from the ambient temperature to 1000−1100°C (Table 4). Each of the developed approaches is characterized by its advantages and disadvantages.

Recent works demonstrate that the most promising approach to improve diamond retention is metallization based on carbide-forming metals, which provides a strong chemical bonding with the diamond surface (Cr, Ti, W, Mo, and others).

Nickeling (non-carbide-forming metal) requires the preprocessing of diamond grains, for instance, in etching solutions or in plasma, to increase the surface roughness, in order to improve the mechanical cohesion of the metal coating with the diamond surface.

ried out at 35−40°C in alkaline solutions concentrated in nickel salts and containing sodium hypophosphite $Na(PH_2O_2)$. After treatment for 1 h, the metallized powders contained 35−45 wt % Ni. Based on the experimental results, it was proposed to introduce into the nickeling solution an additive of the naphthalene sulfonate group in order to accelerate the metal's reduction and produce a nickel coating with low internal stresses.

Table 3. Influence of diamond nickeling on efficiency of drill bits [32]

Metallization rate, %	Mechanical drilling rate, m/h	Average sinking per drill bit, m	Specific consumption of diamonds, carat/m
0	1.5	12.2	1.066
25	1.6	14.6	0.890
50	1.8	19.2	0.677

Table 4. New methods and approaches to diamond metallization

Application method	Precursors	Temperature, °C	Reference
Thermodiffusive metallization	Cr	1000	[9]
Thermodiffusive metallization	Cr	1100	[5−8]
Thermodiffusive metallization	Ti, W	900	[25]
Chemical vapor deposition (RCVD)	$W(CO)_6 + Ni(C_5H_5)_2$		[27]
Iodine transport	Ti, I	600−1000	[10−12]
Microwave heating	TiH_2	760	[15]
Spark plasma coating	Ti		[16]
In Na_2CO_3−NaCl molten salts	W, Na_2CO_3	630−680	[13]
In NaCl−KCl molten salts	WO_3	900−1050	[24]
Chemical reduction of metal ions from solution	$Ni + Na(PH_2O_2)$ salts	35−40	[31]

Coatings based on carbides of hard-melting metals are characterized by hardness, wear resistance, and corrosion resistance; and they protect the materials during operation in various aggressive mediums with abrasive wear [33, 34].

Coatings based on carbides of hard-melting metals also act as an antioxidant barrier preventing the access of oxygen to the diamond surface and its oxidation at higher temperatures. Diamond is oxidized in air at ~700°C. For instance, in [35] the protective antioxidant properties of the Ti−B−C coatings with various contents of boron and carbon were studied. It was demonstrated by thermogravimetry that a TiC coating containing 11 at, % B is characterized by low protective properties: upon heating to 1000°C, it starts losing weight, which is caused by the oxidation of diamond and volatilization of $CO_2\uparrow$. In contrast, TiB_2 coatings containing 60 at % B protect diamond against oxidation in air at 1000°C for over 1 h due to the formation of the B_2O_3 melt as a barrier layer sealing the surface of the diamond grains.

During the operation of tools based on metallized diamonds the diamonds break off from the matrix of superhard materials not in the form of whole grains but gradually according to the mechanism of brittle transcrystalline chipping (minor flakes).

Recent publications of the experimental and commercial tests of new superhard materials demonstrate that diamond metallization both by carbide-forming and non-carbide-forming metals allows improving the efficiency of cutting and drilling tools by over 40–50%.

FUNDING

CONFLICT OF INTEREST

The authors declare to have no conflict of interest.

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