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GEOCHEMISTRY

Mechanochemical Processing of Low-Grade Diamond into Nanocomposite Materials

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Investigation of materials based on diamond [1–5], including methods of mechanochemistry [5], is attracting significant interest. Heat abstraction has become a pressing issue in the semiconductor industry. For example, the amount of heat released from a core of 112 mm^2 in the Intel microprocessor based on the 90-nm technology is more than 100 W. Therefore, improvement of thermal properties of materials used for the preparation of components in microelectronics is a crucial issue. The Advanced Diamond Solutions Company has proposed composites based on copper and diamond [1]. As compared to the conventional materials, such composites have significantly higher heat conductance. The heat-conducting properties of the copper–diamond composite are scrutinized in [2]. According to [3], diamond particles in the copper–diamond composite demonstrate a high degree of resistance to graphitization up to a temperature of 1150–1250 K. Therefore, they can be used for the construction of high-current electric contacts in low-voltage equipment. According to the technique of nanocomposite preparation described in [4], diamond particles of the final product can be sputtered with ~10-nm-thick nickel coating using plasma pulverization technology.

The aim of the present paper is to elaborate scientific principles for obtaining functional materials with high heat-conducting properties based on the diamond–graphite–copper composite using the method of abrasive-reactive wear on the steel milling tools of mechanochemical reactors [5]. Let us substantiate the validity of the application of graphite. First, graphite can substitute for expensive diamond (in this case, even a small amount of diamond material can be sufficient for initiating nanowear). The heat conductance of diamond (1200–2000 W/m K) at room temperature is approximately four times higher than that of copper (380 W/m K). The heat conductance of graphite can drop to 300 W/m K depending on its density. This parameter can be as low as 500 W/m K for natural graphite and 2400 W/m K for pyrographite (graphite can be transformed into pyrographite in mechanochemical reactors [6]).

We used AGO-2 and EI-2 × 150 two-drum planetary centrifugal mills to carry out the mechanical activation. In order to realize the task formulated above, we constructed rod duralumin drums adapted for utilization in both milling tools. The drums were equipped with cylindrical inserts made up of rod copper. The parameters of the inserts are as follows: internal radius $l_2 = 1.9$ cm; height $h = 5.6$ cm; and volume $V \approx 60$ cm^3. The movable milling tools were prepared from 2-mm-thick sheet copper. In the copper insert 1 (mass $M_1 = 401.16$ (bucket) + 127.46 (lid) = 528.62 g), the mass of movable bodies was chosen equal to $m_1 = 100.39$ g, $N_1 = 275$, and their average radius $r_1 = 0.2135$ cm. The respective values for insert 2 are as follows: $M_2 = 358.15 + 128.44 = 486.59$ g, $m_2 = 140.21$ g, $N_2 = 323$, and $r_2 = 0.2261$ cm. The equality of the masses of the two drums in the set was provided by m_2 or N_2.

For experiments, we used technical-grade natural diamond crystals (up to 1 mm in size) from kimberlitic pipes of the Yakutian diamondiferous province and graphite powder of the specific purity grade.

The diamond crystals were finely ground in a Fritsch Pulverisette mill equipped with steel furniture (mortar diameter 9.45 cm + ball diameter 5.16 cm) up to a dimension of less than 50 μm (control under optical microscope). After treatment with hydrofluoric acid and aqua regia to remove impurities, diamond crystals were subjected to decantation from deionized water.

The purified, washed, and dried diamond powder (3 g) was used to prepare the copper–diamond composite in copper insert 1, while a mechanical mixture of diamond (1.5 g) and graphite (1.5 g) powders was used to prepare the copper–diamond–graphite composite in insert 2. In order to scrutinize wear of the copper lid of the insert by optical microscopy, insert 2 was installed upside down (i.e., lid at the bottom) inside the drum.

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The mechanical activation time in an EI-2 × 150 mill was set at 210 min at the relative collision velocity of the copper milling tools

$$W = 2\pi\omega_1 l_2[(k+1)^2 + m^2 - 2m(k-1)\cos\varphi + (m+1)^2]^{0.5} \approx 7 \text{ m/s}. \quad (1)$$

Here [5, 7], $m = l_1/l_2 = 4.7/1.9 = 2.5$ is the geometrical factor ($l_1 = 4.7$ cm is the distance between rotation centers); $k = \omega_2/\omega_1 = -1$ is the kinematic factor; $\omega_2 = \omega_1 = |\omega| = 14$ s^{-1} is the pole rotation frequency; and $\cos\varphi = -(1 + k)/m = 0$ determines the angle of ball breakaway from the insert wall. Mechanical activation was performed in an airproof condition with a vacuum pad. After the first 10 min of mechanical activation, the drums were opened and checked visually for the activation state of powder and copper milling tools. The walls of the copper insert turned out to be coated with the activated powder. The surface of the partly rolled movable milling tools remained pure, but they acquired a slightly gray color. Subsequently, mechanical activation was carried out for 200 min with ~15-min-long intervals after each 20 min of mechanical activation to provide the cooling of drums.

Compositions and structures of samples were studied by gravimetry, Raman spectroscopy (Dilor/OMARS), X-ray phase analysis (DRON-3), differential thermal analysis (Q-1000), optic microscopy (NU-2E), and scanning microscopy (JSM-6380 and LEO-1550).

The results of the experiment demonstrated both similarities and dissimilarities of mechanical activation only for diamond (sample 1) and the diamond–graphite mixture (sample 2). The mechanical activation of sample 1 yielded a dark powder. Sample 2 yielded both powder and pale compact material on the walls of the copper insert. In both cases, the movable copper milling tools were subject to rolling: copper parallelepipeds were transformed into flattened ellipsoids. However, contrary to expectations, their wear δ after the mechanical activation of sample 1 appeared nearly one order of magnitude lower than that of sample 2: $\delta = m_1 - m_1^* = 100.39 - 99.69 = 0.70$ g; $\delta_2 = m_2 - m_2^* = 140.21 - 133.94 = 6.27$ g (m^* is the weight after run). In contrast, the mass discrepancy Δ of inserts increased rather than decreased after the separation of the activated product from the walls of the inserts (buckets and lids) and the mechanical cleaning of their surfaces from the product. For example, after the mechanical activation of sample 1, the mass of the bucket increased by 401.86 – 401.16 = 0.70 g, while mass of the lid increased by 127.5649 – 127.4632 ≈ 0.10 g. Thus, Δ_1 is equal to –0.80 g. For sample 2, the respective values are 359.05 – 358.15 = 0.90 g and 128.7150 – 128.4440 ≈ 0.27 g. Δ_2 is equal to –1.17.

Examination of working surfaces of milling tools with optical microscopy showed that the increase in mass of the copper insert is related to the phenomenon of hardening, i.e., nonuniform penetration of solid diamond particles (sample 1) or the diamond–graphite mixture (sample 2) into the working layer of inserts. Moreover, holes and bands (filled with products of mechanical activation) left by diamond particles on walls of inserts dominated (in terms of number and volume) over the implanted diamond particles. This phenomenon hampered the determination of the exact composition of the newly formed composites by the weight analysis. For example, based on the masses of milling tools weighed before and after the mechanical activation of sample 1, the composite corresponds to a diamond content of 75.8% (correspondingly, the Cu content is 24.2%). After the mechanical activation of sample 2, the content of carbon (diamond + graphite) in the composite was 22.6% and the Cu content was 77.4%.

We could solve this problem by X-ray phase analysis (Fig. 1), Raman spectroscopy (Fig. 2), and differential thermal analysis (Fig. 3). The powder XRD data on diamond, graphite, and their mixture (1: 1) were identical with PDF 79-1467 for diamond, PDF 12-212 for graphite, and the superposition of both patterns for the mixture. After the mechanical activation of samples, the XPA data virtually did not differ under identical measurement conditions (Fig. 1): reflections of graphite disappear (graphite is transformed into the amorphous state [5, 6]); diamond crystals remain in the crystalline state, but the reflections are strongly masked by reflections of nanowear particles of the copper furniture of milling tools; hence, the mechanical activation of both samples does not produce carbon and copper compounds (it is well known that copper does not react with diamond) and the newly formed composites have a copper–carbon phase composition. Let us note that products of the mechanical activation of samples can arbitrarily be divided into three subspecies: subspecies 1 (powder); subspecies 2 (0.*n*-mm-thick compact layer with a concave internal surface); and subspecies 3 (similar to subspecies 2 but with a convex external surface adjacent to the copper insert wall).

In the case of mechanical activation of sample 2, the compact layer can partly be recovered manually from the insert wall. However, it is possible only with a lathe in the case of sample 1. Raman spectrometric data on the starting diamond and its product (Fig. 2) indicate that mechanical activation does not create chemical bonds between copper and carbon atoms (Cu–C bonds). Instead, graphite is transferred to the amorphous state. However, the nature of the minor shift of oscillating modes of diamond to lower frequencies in the case of mechanically activated powder samples 1 and 2 (subspecies 1) remains unclear. Analysis of samples 1 and 2, as well as the control sample (powder mixture of diamond, graphite, and copper), in atmosphere by the DTA method (thermogravimetry, heating rate 10°C/min) yielded important information (Fig. 3). The results show that a significant variation in the sample mass begins at $T >$ 700°C (burning of diamond) for sample 1 and at $T >$ 100°C (burning of amorphous carbon) for sample 2

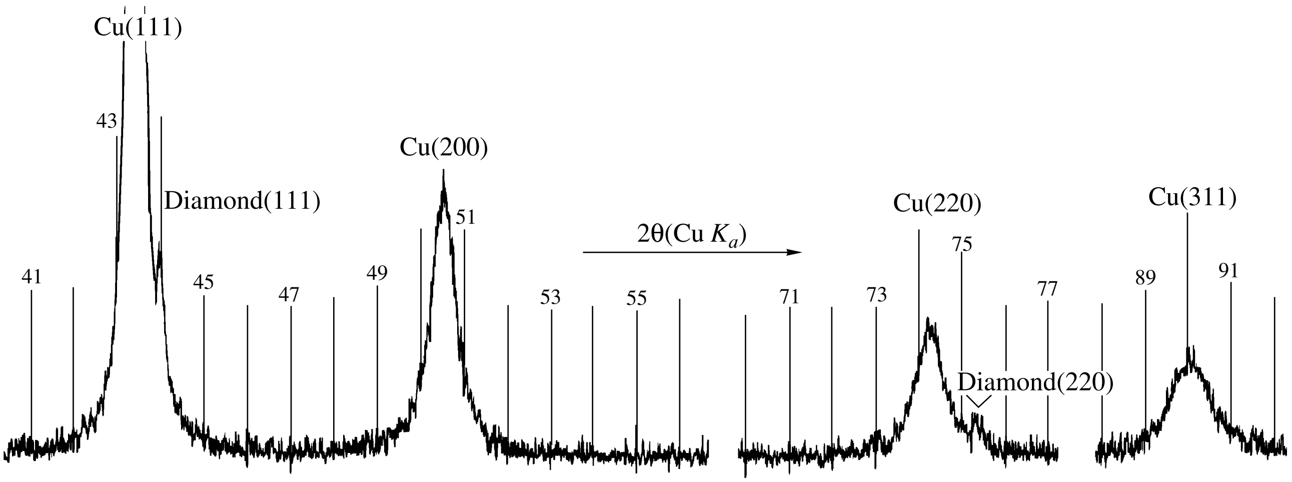

Fig. 1. X-ray phase analysis of the product of mechanical activation of diamond (weight 3 g) for 210 min in an EI-2 × 150 mill with Cu furniture (average radius of milling tool $r_1 = 0.2135$ cm and its number $N_1 = 275$).

(Fig. 3). Based on a thermogravimetric pattern similar to that in Fig. 3, the mass of the control mixture also increases markedly due to oxidation at $T \sim 1000$°C (the presence of carbon creates a reducing environment in the crucible and hampers the oxidation of copper). Therefore, the thermogravimetry data can be used to decipher constituents of composites. For example, based on the thermogravimetry data (Fig. 3), the composite in sample 2 includes 24% carbon (7.3% amorphous carbon and 16.7% diamond). Hence, the Cu content should be 76%, which is very close to the weight analysis data. For comparison, the thermogravimetry data indicate that the mechanically activated product in sample 1 contains 77% diamond and 23% copper. Thus, efficiency of the production of pure copper–diamond composites (sample 1) by the method of abrasive-reactive wear on the milling tools of mechanochemical reactors is inferior than that of the method based on copper–diamond–graphite composites (sample 2) due to the prominent phenomenon of hardening that hampers the process of wear. Therefore, mainly the results obtained in the graphite-bearing system (sample 2) are discussed below.

Data on the microanalysis of different points of sample 2 confirmed qualitatively the XPA data. In terms of quantitative assessment, the images obtained indicate the presence of some heterogeneity in the distribution of carbon. Light-colored areas correspond to C-rich zones, while dark areas indicate C-poor zones. The images also show areas with an intermediate composition.

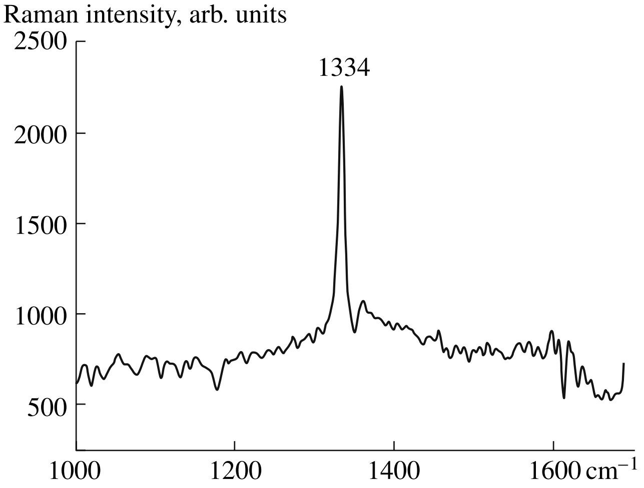

Fig. 2. Raman spectrum of the mechanically activated sample 2 (subspecies 2).

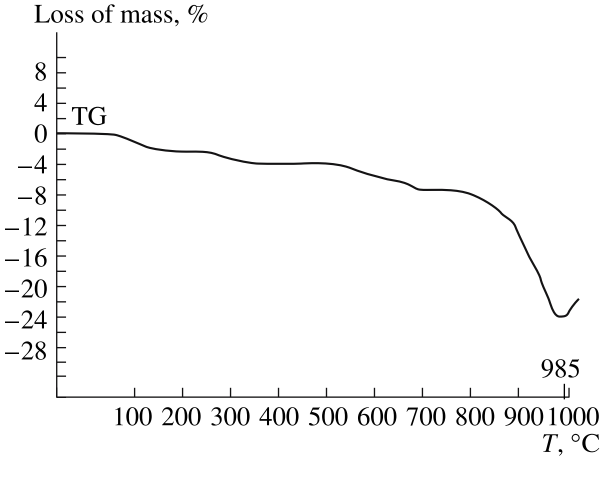

Fig. 3. Thermogravimetry of the diamond (1.5 g)–graphite (1.5 g) system in the atmosphere of the product of mechanical activation for 210 min in an EI-2 × 150 mill (radius of milling tools $r_2 = 0.2261$ cm, $N_2 = 323$).

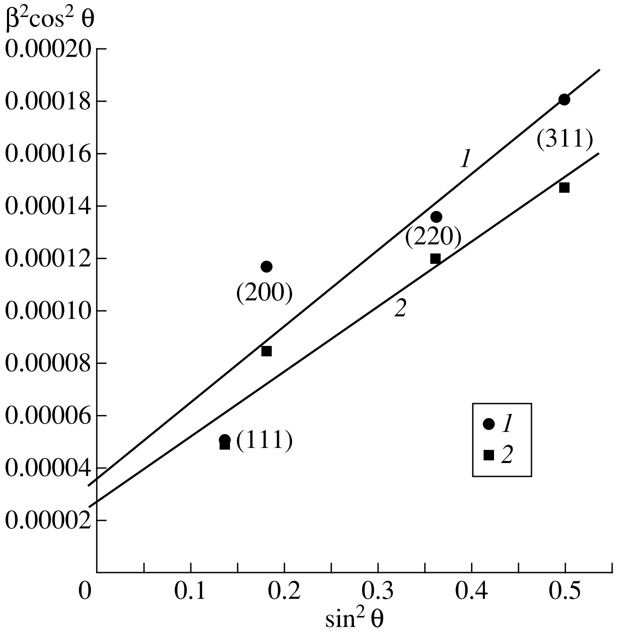

Fig. 4. Results of processing of the XRD data on Cu reflections by the Williamson–Hall method. (*1*) Sample 1; (*2*) sample 2 (subspecies 1).

SEM images of the surface of the compact product of mechanical activation facing the movable milling tools (subspecies 2) show that the copper–diamond–graphite composite mainly includes agglomerates 5–10 μm in size. The reverse side (subspecies 3) virtually represents a compact material with the internal structure composed of the same aggregates of particles. Higher resolution (2 and 1 μm) images show that the agglomerates can be composed of particles much smaller than 1 μm. Thus, we can affirm that mechanical activation of the diamond–graphite mixture can yield massive composite samples even without the high-pressure annealing [4] of the product of mechanical activation.

In order to determine the characteristics of the state of copper in the mechanically activated powder samples 1 and 2, we processed the XPA data using the Williamson–Hall plot [8, 9]:

$$\beta^2\cos^2\theta = \Lambda/D^2 + 16\varepsilon^2\sin^2\theta, \qquad (2)$$

where β is the broadening of reflections of Cu after the subtraction of the individual broadening of reflections of the standard (carbonyl silicon), $(\Lambda/D)^2$ is the Y-intercept, $\Lambda = 0.15418$ nm is the wavelength of the CuK_α radiation, and D is the dimension of Cu crystallites. Tangent $\tan A = 16\varepsilon^2$ of slope A of straight lines *1* and *2* yields the microstrain ε value of crystallites. Processing of data in Fig. 1 and materials pertaining to the analogous (in terms of mechanical activation) sample 1 yielded the following results (Fig. 4):

sample 1 (copper–diamond system): $D_1 = 262$ Å ≈ 26 nm, $\varepsilon_1 = 0.0043$ (0.43%);

sample 2 (copper–diamond–graphite system): $D_2 = 295$ Å ≈ 30 nm, $\varepsilon_2 = 0.0039$ (0.39%).

Based on the high-resolution SEM data, the relatively large agglomerates of particles have a cauliflower-type internal structure with block dimension similar to certain dimensions of Cu crystallites.

The results of the mechanical activation of diamond and the diamond–graphite mixture suggest that graphite can be used to produce a nonautonomous phase [10] of amorphous carbon on the surface of other particles of the composite. Study of several physicochemical properties of composites demonstrated that the nonautonomous phase has a significant influence on the process of mechanical activation. In particular, the formation of amorphous carbon enhances the degree of nanowear of the copper material of milling tools by nearly one order of magnitude.

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