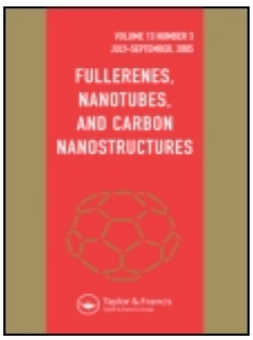

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Processing of Detonation Diamonds with Metal-Containing High-Frequency Arc Plasma and Their Properties

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This paper describes coating of diamond powder with metal by plasma. Arc plasma was generated in double jet high-frequency argon-operated plasmatron with atomized metal inserts. The diamond powder was added to the plasma in a flow of helium. Copper and nickel coated particles of detonation and industrial diamonds were studied by XRD, XPS, SEM methods and electron magnetic resonance. Results of these studies are presented.

Keywords Nanodiamond, nanoparticle, metal-containing plasma

Introduction

Fine particles of diverse allotropes of carbon with metal coating are widely used as catalysts (1). Metal coating deposited on the particles of industrial diamond produces stronger processing tools. Ni, Co and Fe metals are used as catalysts to produce industrial diamonds by high-pressure high-temperature synthesis (2). In most cases, it is essential to deposit the metal as homogeneously as possible. Particles with structure "nucleus material with one band gap, coating material with a different band gap" display properties of an atom, that is, have an intrinsic level system. Metal coating is generally deposited on a particle by chemical or electrochemical methods. It is common knowledge that the nanodispersed particles exist as clusters and are bigger than the individual particles they comprise. In the arc plasma of inert gas, the clusters can be assumed to dissociate into individual particles; as they cool the atoms of metal contained in the plasma condense on their surface to form the metal coating. Then the particles already coated with metal again coagulate to form clusters.

The work describes our method of plasma deposition of copper and nickel coating on industrial and detonation diamonds (3) and presents results of their analysis.

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Experimental

The arc plasma was generated in a double jet plasmatron placed inside a sealed water-cooled chamber. The electrodes of the plasmatron were copper water-cooled rods with removable atomized metal inserts (nickel, copper) and had an axial bore through which the plasma-supporting gas, argon, was fed. The angle between the electrodes was 90°. Diamond powders were supplied by a special device from below through a quartz tube together with the transport gas, helium, into the area where the discharges merge (4). Electric power supply circuit of high-frequency arc plasmatron was identical with that described in (5). Synthesis parameters were discharge current–15 A, voltage on the electrodes–170 V, frequency–66 kHz, plasma-supporting gas flow rate–6 l/min, transport gas flow rate–8 l/min and diamond powder flow rate–250 mg/min. Diamond powder samples were annealed in hydrogen flow at 700°C for 20 minutes.

The temperature of plasma jet and plasmatron erosion were studied by atomic emission spectral analysis. The temperature calculated by the method of relative spectral line intensities of copper at every point of plasma jets from the electrode ends to the point where the jets merged was 6800 K. From the point of merging upward it smoothly decreased, and at 50 mm from the point the temperature was 4835 K. Erosion of the electrodes was evaluated by weighing the electrodes and by copper (nickel) concentration by line intensity and concentration curve; for the copper electrodes it was $1.2 \cdot 10^{-8}$ kg/C and for the nickel electrodes, $0.7 \cdot 10^{-8}$ kg/C.

X-ray fluorescence analysis of the samples was done with Pioneer S4 Bruker spectrometer. X-ray diffraction (XRD) analysis of the samples was performed with DRON-4 automated powder diffractometer, X-ray tube radiation Cu K_a. X-ray photoelectron spectroscopy (XPS) studies were carried out with SPECS GmbH ultra-high vacuum photoelectron spectrometer and X-ray tube radiation Al K_α. Samples were analyzed after their surface was etched for 5 minutes with Ar ion beam (1 keV, 30 mA). Scanning electron microscopy (SEM) of samples was carried out with SEM Hitachi S-5500 high-resolution microscope. X-ray microspectral analysis was carried out with NSS 7 energy-dispersion spectrometer. Magnetic properties of the samples were studied with Elexys E580 Bruker Fourier-transform spectrometer.

Results and Discussion

The X-ray diffraction pattern of a detonation diamond sample exhibits two diffraction maxima at angles 43.8° and 75.4° (Figure 1, curve 1). The average size of diamond crystallite was determined by Scherrer formula. The detonation diamond was sized 45 Å. Plasma processing of detonation diamond decreased intensities and broadened the diffraction maximum lines corresponding to the diamond structure, that is, decreased the crystallite size to 35–40 Å. The XRD pattern of a detonation diamond processed in nickel-containing plasma displays low-intensity reflections of NiO oxides (37.1, 43.2, 62.6, 75.1 and 79.1°) and Cu_2O oxides (36.4, 42.3, 61.4 and 73.5°) (Figure 1, curve 2). Nickel and copper content in this sample was 0.6 and 0.3 wt%, respectively. Copper in the plasma-processed samples depends on its content in the nickel electrode inserts in the amount of 3wt%. The X-ray diffraction pattern of a detonation diamond sample processed in copper-containing plasma exhibits reflections of two copper oxides — CuO (35.5, 38.8, 48.8, 58.4, 61.6, 66.3, 68.1 and 75.2°) and Cu_2O (36.4, 42.3, 61.4 and 73.5°) (Figure 1, curve 4). Copper content in the sample was 4.4wt%. Oxides in all plasma processed samples are present because we used commercial argon (GOST 10157-79) containing impurities of pure oxygen and

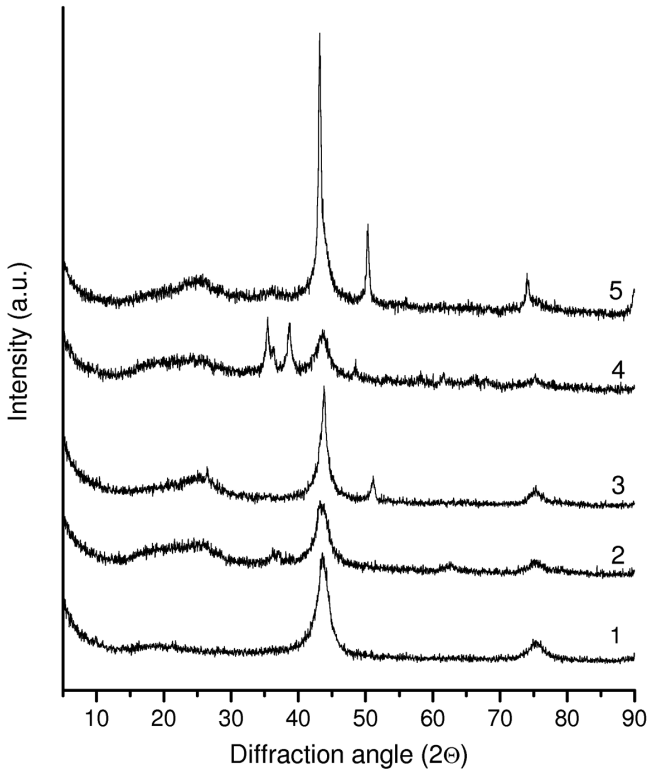

Figure 1. XRD of samples: 1 – detonation diamond; 2 (4) – detonation diamond, processed in nickel (copper)-containing plasma; 3 (5) – detonation diamond, processed in nickel (copper)-containing plasma annealed in H_2.

its compounds. Annealing of detonation diamond samples in hydrogen flow increased intensities and decreased line widths of diffraction maxima corresponding to the diamond structure, that is, increased the crystallite size to 60–70 Å. After annealing in hydrogen flow, in addition to reflections corresponding to diamond structure, the XRD patterns of detonation diamond samples exhibit reflections of Ni (44.4, 51.7 and 76.1°) and Cu (43.3, 50.5 and 74.2°), corresponding to the material of electrode inserts (Figure 1, curves 3 and 5). After annealing of samples processed in nickel (copper)-containing plasma the content of nickel (copper) in the sample was 2.4wt% (3.2wt%).

The detonation diamond sample, processed in nickel-containing plasma, was studied by the XPS method before and after annealing in hydrogen flow. Distribution of bond energy of the line in the detonation diamond sample made possible the identification of hybridization of pure carbon sp^2 and sp^3 (15 and 65% of the area of C 1s line, respectively) and also the definition of C=O and C–O–C bonds (18% and 2% C 1s, respectively) (Figure 2a). Due to the decomposition of Ni 2p line, only 30% of nickel in the sample is in the oxidized state (Ni–O), and the remaining 70% account for metal nickel. After this the sample was annealed, and the decomposition of C 1s line made possible the finding that part of the carbon in sp^3 hybridization was 92%; oxidized carbon was 8% (Figure 2b). Ni 2p line corresponded to metal nickel.

From Figure 3a it is apparent that the detonation diamond sample processed with nickel-containing plasma exhibits particles of nanodispersed diamond sizing 5–7 nm.

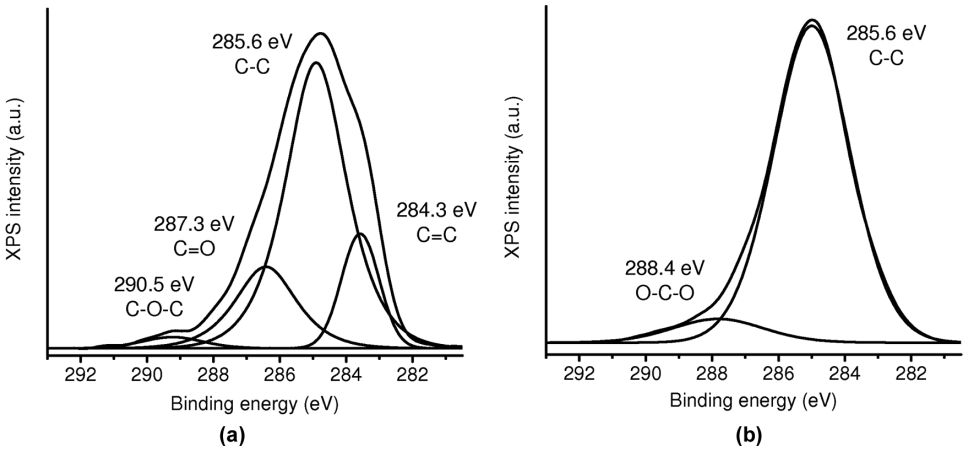

Figure 2. XPS spectra of C 1s line for a sample of detonation diamond processed in nickel-containing plasma before (a) and after annealing in hydrogen flow (b).

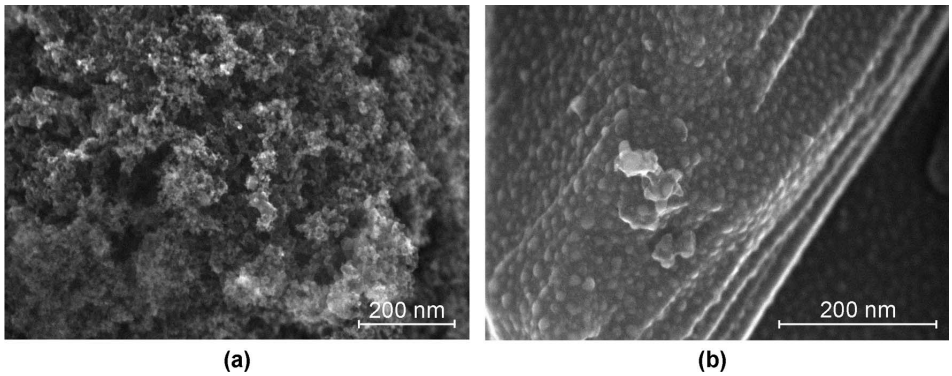

Figure 3. SEM micrographs of samples processed in nickel-containing plasma: (a) detonation diamond and (b) fine-dispersed diamond.

No nickel particles are observed, even though the X-ray microspectral analysis shows its presence in the amount of 0.56wt%. Figure 3b shows a typical particle of fine-dispersed diamond processes with nickel-containing plasma sizing 2.1 μm, coated with nickel particles sizing 8–14 nm.

Electron magnetic resonance shows that annealing of detonation diamond samples processed with copper-containing plasma decreases the contribution of dispersion of magnetic susceptibility due to decreased size of magnetic particles. Annealing of detonation diamonds processed with nickel-containing plasma does not change the dispersion of magnetic susceptibility. The temperature dependencies of electron magnetic resonance lines in plasma-processed detonation diamond samples also show that the size of nickel particles is substantially smaller than the size of copper particles. Plasma processing of detonation diamond changes the g-factor of the radical from 2.0036 to 2.0028, and in annealing in hydrogen flow its value is 2.0019. This proves the changes in the bonds of surface atoms in the detonation diamond with the metal atoms on its surface.

Conclusions

Injection of diamond powder into the arc plasma of double jet plasmatron has been shown to produce particles coated with the metal of electrodes. Processing of detonation diamond with nickel or copper-containing plasma forms on the surface of the detonation diamond nickel particles with size substantially less than the size of copper particles. Annealing of diamond powders processed in nickel or copper-containing plasma reduces nickel and copper to a metal state. Annealing also changes the allotropic state of carbon, and almost all carbon is recorded in sp^3 hybridization (92%). The size of diamond crystallites increases from 35–40 Å to 60–70 Å.

Acknowledgments

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References

1. Lisitsyn, A.S., Parmon, V.N., Duplyakin, V.K., and Likholobov, V.A. (2006) Modern problems and prospects of deposited palladium catalyst studies. *Russ. Him. J.*, L: 140–153. (in Russian)
2. Aleksenskiy, A.E., Yagovkina, M.A., and Vul', A.Ya. (2004) Intercalation of ultrafine-dispersed diamond in aqueous suspensions. *Phys. Solid State*, 46: 685–686.
3. Chiganov, A.S. (1997) Separation of ultradispersed diamonds from products of detonation synthesis. *Russ. J. Appl. Chem*., 70: 1458–1461.
4. Churilov, G.N., Lopatin, V.A., Novikov, P.V., and Vnukova, N.G. (2001) A technique and device for studying alternating-current discharge dynamics. Stratification of a discharge in an argon flow at atmospheric pressure. *Instrum. Exp. Tech*., 44: 519–523.
5. Churilov, G.N. (2008) Source of light for spectral analysis. RU Patent 2326353 C1, G01J3/10.