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EFFECTS OF ULTRASONIC TREATMENT ON AQUEOUS SUSPENSIONS OF DIAMOND NANOPOWDERS

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It has been found that ultrasonic treatment of diamond nanopowders contributes to surface cleaning due to the removal of non-diamond carbon and impurities from the surface boundary of nanodiamond grains (from 0.4 and 0.32 % for ASUD-99 and 0.67 and 0.55 % for ASUD 75, respectively). It does not affect the total sorption volume and the values of the specific surface of the studied samples do not change, but it changes the composition of groups on the surface of diamond nanoparticles, which affect its hydrophilicity.

In the samples of ASUD-75 after ultrasonic treatment, a redistribution of the ratio of the intensities of valence vibrations of C=O bonds in the lactone (anhydride) group (1742 cm^{-1}) and the quinone (carboxyl) group (1683 cm^{-1}) is observed, which indicates the decay of the lactone ring and its transformation into carbonyl and carboxyl groups. All samples of ASUD-99 have a hydroxyl group O-H (3400 cm^{-1}), which does not change significantly under the influence of ultrasound. This explains the noticeable change in agglomeration for ASUD-75 in contrast to ASUD 99.

***Keywords**: diamond nanopowders, ultrasonic treatment, impurities, composition of groups on the surface, hydrophilicity*

INTRODUCTION

Carbon is a chemical element that can form several allotropes in which the carbon atoms are in certain states described as *sp*^{3}-, *sp*^{2}-, and *sp*-hybridization of atomic orbitals. Diamond is a form of polycarbon substance formed by carbon atoms in a state of *sp*^{3}-hybridization, with a molecular structure in the form of a three-dimensional grid. The dimensions of diamond macromolecules are determined by the size of its single crystal particles and can take on values from several angstroms to several millimeters or centimeters when transiting from nanodiamonds (ultradisperse detonation diamonds – UDA) to single crystals [1–3].

The nature and density of the diamond's functional coating determine its properties. At the same time, the share of surface atoms in the total number of carbon atoms, which determines their contribution to the properties of a diamond, depends on the size of its macromolecules. It is especially large for nanosized diamond particles. For example, in UDA, as the calculation shows, the mass of functional groups can be compared with the mass of the polycarbon core. Any action on a diamond begins with an impact on its functional coating, so the chemical state of the diamond surface can affect both the specifics of the impact and the final result.

Interacting with oxygen at elevated temperatures of 400–500 °C, carbon absorbs from 15 to 25 % of oxygen, a significant portion of which is firmly bound to the surface in the form of protogenic groups, represented in most cases by heteroatoms of hydrogen and oxygen, which significantly affect the adsorption properties of carbon materials. Functional groups can be considered by analogy with the functional groups of aromatic compounds known from organic chemistry [4]. The simplest in structure are carboxyl, phenolic and quinone groups [5]. When two carboxyl groups interact, an anhydride group can be formed, and when a carboxyl and phenol group interact, a lactone group can be formed. There are also other types of groups on the surface of carbon materials - hydroxyl, hydroperoxide, carbonyl, ether and others, but their content is insignificant. Surface groups play a key role in the adsorption of components from the liquid (aqueous) phase and are responsible for the catalytic properties of the surface [6].

It is known that any manipulation of the surface leads to its modification. One of the well-known methods of cleaning diamond powders from surface impurities and reducing surface energy is ultrasonic treatment (UT). In works [7, 8], the influence of ultrasound on the physicochemical properties of synthetic diamond nanopowders of detonation synthesis was considered. It was found that ultrasonic radiation leads to a reduction of active groups and centers on the surface of nanodiamond powders (contributes to surface hydrophobization) and significantly affects their heat resistance. A more noticeable change in agglomeration for ASUD-75 in relation to ASUD-99 under the action of ultrasound is not fully justified. Therefore, the purpose of this work was to study the effect of ultrasound on aqueous suspensions of diamond nanopowders of the ASUD-75 and ASUD-99 brands (with a diamond phase content of 75 and 99 %, respectively).

RESEARCH MATERIALS AND METHODS

ASUD-75 (ultradisperse synthetic diamond with a diamond phase content of 75 %) and ASUD-99 were used as starting materials. To study the effect of ultrasound (frequency of 35 kHz) on the physical and chemical properties of detonation synthesis nanodiamond powders, the samples were placed in a cylindrical flask with a lid, distilled water, and treated for 30 min. After that, the solution was dried to a constant mass for 36 h at the temperature of 150 °C.

The state of the original UDA surface was studied by electron microscopy and X-ray spectral microanalysis with software-digital image processing using a ZEISS EVO 50XVP electron microscope equipped with energy dispersive X-ray spectrum analyzers for elemental analysis. The ZEISS EVO 50XVP microscope has a resolution of up to 2 nm and the capability to work under low vacuum, to perform elemental analysis with an error of ~ 0.1 % in the range from boron to uranium, it is equipped with an HKL CHANNEL 5 system for electron diffraction from a local area larger than 10 nm of the company OXFORD.

X-ray studies surface of the UDA was performed on a DRON-3 X-ray diffraction apparatus with a slit width of 1 mm on the collimator and 0.25 mm on the detector. In order to avoid the ingress of extraneous amorphous impurities into the studied powder, the photographing was carried out in aluminum foil. That is why there are peaks of aluminum in X-ray images.

The analysis of ash residues in the original powders and treated by ultrasound in the form of unburned residue was determined according to the method [9].

The pore size distribution of the original UDA samples was determined by the nitrogen adsorption method at –196 °C using a Quantachrome NovaWin2 device. Before the research, the samples were degassed at 180 °C for 20 h in a vacuum, which ensured the removal of all physically adsorbed substances from the surface. The specific surface area (S) of the samples was determined by the BET method, the total pore volume (V_S) was calculated by the amount of nitrogen adsorption at $p/p_S = 0.99$, and the pore distribution was determined by the DFT (density functional theory) method.

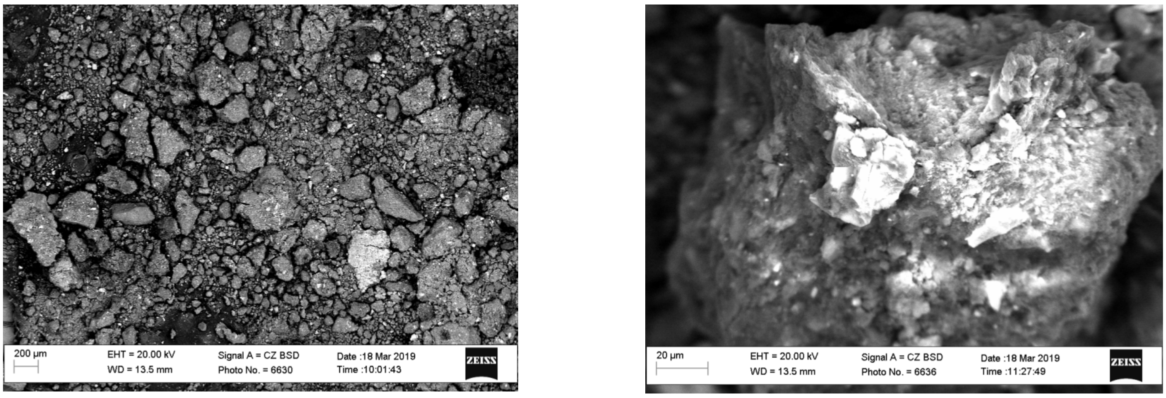
Fourier transform infrared spectroscopy (FTIR) on a Nicolet 6700 spectrometer with a Nicolet Continuμm IR microscope coupled to it was also used to identify functional groups on the surface of the studied UDA samples. To study the composition of functional groups and its changes, as a result of various types of processing, the method of impaired total internal reflection (PPVV ATR) and methods of registration of diffuse reflection spectra (DRIFT) were used. Such research methods allow obtaining a signal directly from the surface of a solid sample and do not require special sample preparation.

RESULTS OF STUDIES

Electron microscopic studies have found that the particles of the original UDA have the appearance of flakes of different sizes and varying degrees of continuity (Fig. 1). Almost all particles are characterized by a multi-level microstructure. The first level is monocrystalline grains with a size of 2–10 nm. The second level is the joining of particles of close orientation. The third level is large aggregates based on agglomerated and individual UDA grains. The dimensions of such a layer reach 30–40 nm.

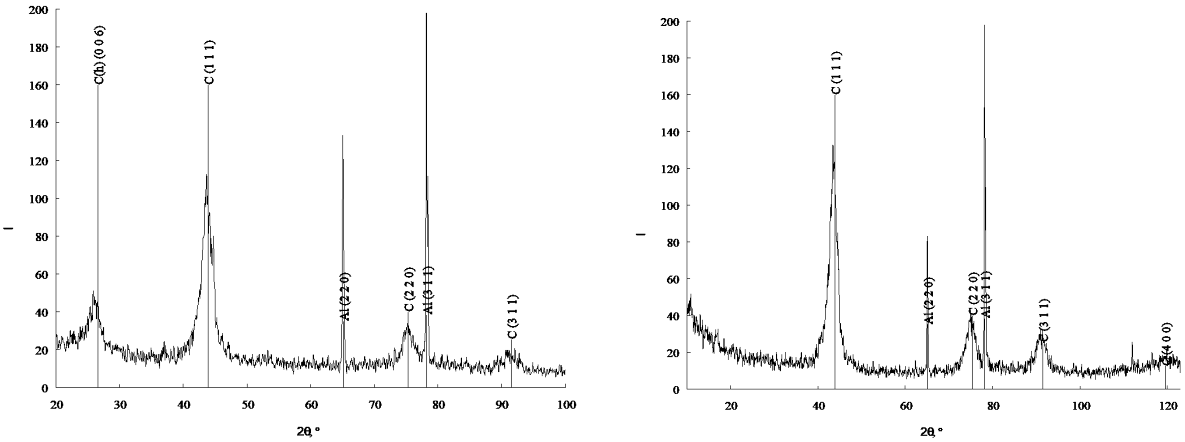
X-ray patterns for initial samples ASUD-75 and ASUD-99 are shown in Fig. 2. Both samples have the same background shape, which is characteristic of fine-crystalline samples. The diamond peaks have almost the same shape, no “amorphous halo” characteristic of amorphous substances is observed. The lattice parameter was calculated from the positions of the diamond peaks. For ASUD-75 and ASUD-99, it is approximately 3.583 Å, (the maximum measurement error was ± 0.00135 Å). As can be seen, the lattice parameter does not change from sample to sample, but it is slightly larger than the reference 3.5667 Å, meaning that the diamond grain contains impurities. Determined by the Debye-Scherrer formula, the average diamond crystal size is approximately 7.2 nm.

From the data shown in Fig. 2, it can be seen that, unlike ASUD-99, there is a small admixture of graphite in the initial sample of ASUD-75. The presence of a broad peak indicates the nanodispersity of the graphite admixture. The structural heterogeneity of the surface of ASUD-75 (the presence of sp^2- hybridization of atomic orbitals) opens up the possibility of creating a wider range of surface-containing oxygen groups grafted to different parts of the carbon matrix.



a *b*

Fig. 1. SEM images of initial UDA: magnification 70 (*a*), 15 000 (*b*)



a *b*

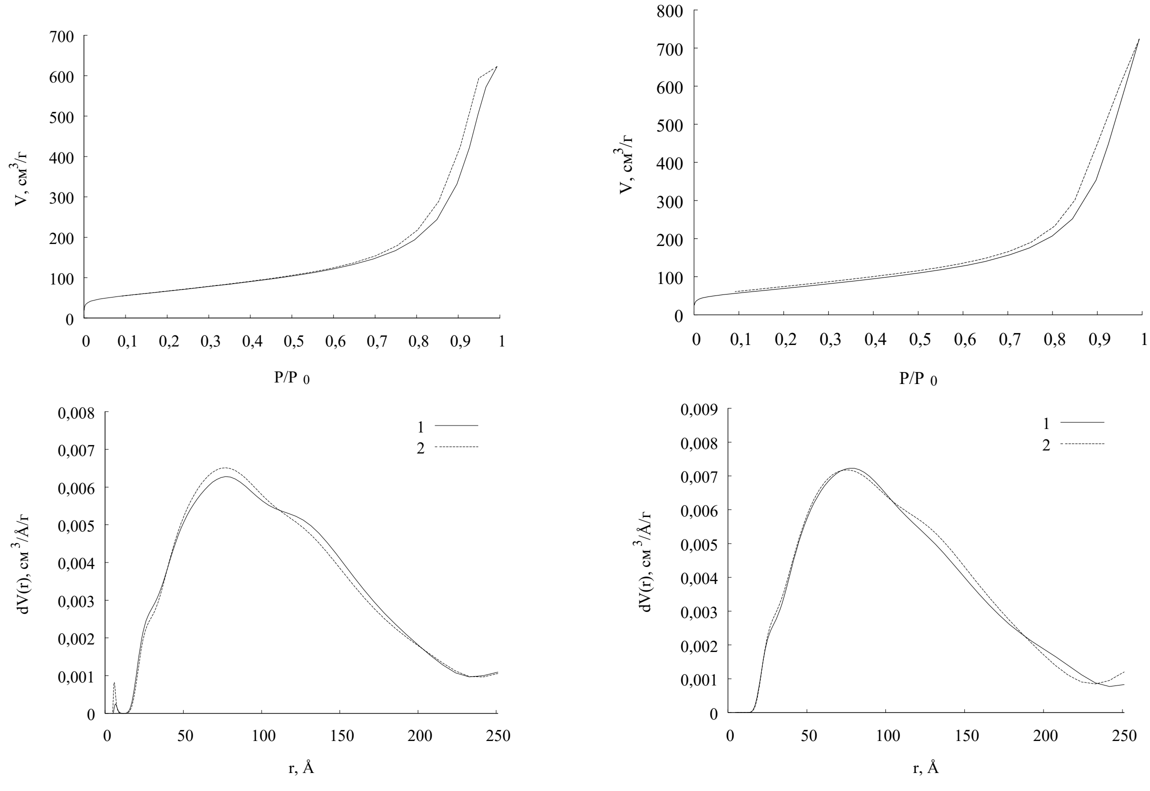
Fig. 2. X-ray patterns for initial samples ASUD-99 (*a*) and ASUD-75 (*b*)

Nitrogen adsorption isotherms on ASUD-75 and ASUD-99 have a similar shape. The studied samples are characterized by low adsorption in the region of low p/p_0 values, which is explained by the small content of micropores in the porous structure. The volume of micropores determined by the Dubinin-Radushkevich equation is the same for these samples and is 0.086 cm^3/g. A large hysteresis is observed on the isotherms of these samples, which indicates the presence of mesopores in the porous structure. The volume of mesopores, defined as the difference between the total sorption volume and the volume of micropores, is 0.877 and 1.033 cm^3/g for ASUD-75 and ASUD-99, respectively. Thus, the studied samples belong to mesoporous materials, their specific surface area, determined by the BET method, is characterized by close values and is 215 and 232 m^2/g, for ASUD-75 and ASUD-99, respectively.

Fig. 3 shows nitrogen ads.-des. isotherms and dependence of pore size distribution with respect to the pore volume, the sizes of the initial samples ASUD-75 and ASUD-99 and after ultrasonic treatment. As can be seen from the figures shown in Fig. 3 data, ultrasonic treatment does not significantly affect the total sorption volume. For the tested samples, the values of the specific surface do not change (216 and 232 m^2/g, for ASUD-75 and ASUD-99, respectively).

In fact, ultrasound promotes a thermodynamically beneficial process of aggregation of micrometric particles, which is accompanied by a decrease in the free surface energy of the system, inhomogeneity of aggregated nanoparticles, and surface cleaning due to the removal of non-diamond carbon and impurities from the surface boundary of nanodiamond grains. Thus, the analysis of ash residues in the original powders and treated by UT in the form of unburned residue showed a different amount of impurities in the original powders and those treated by UT, respectively, 0.4 and 0.32 % for ASUD-99 and 0.67 and 0.55 % for ASUD-75 The removal of non-diamond carbon is facilitated by thermal oxidation below 550 °C, while the diamond part remains unchanged.

A more noticeable change in agglomeration for ASUD-75 compared to ASUD-99 under the influence of ultrasound [7, 8] probably can be associated with a change in oxygen groups on the surface of diamond nanoparticles. Fig. 4 shows the IR spectra of ASUD-99 and ASUD-75 before and after ultrasound.



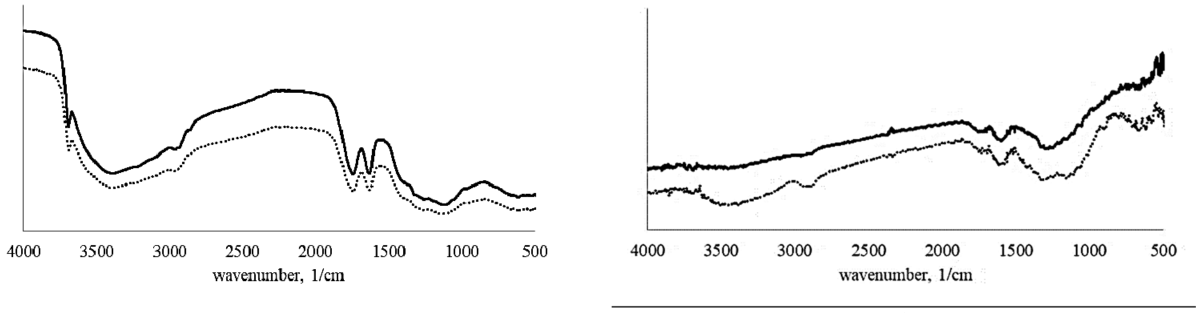
a *b*

Fig. 3. Nitrogen ads.-des. isotherms and dependence of pore size distribution with respect to the pore volume the sizes of the initial samples (solid) ASUD-75 (*a*) and ASUD-99 (*b*) and after ultrasonic treatment (dashed)

Fig. 4 shows that ultrasound has a greater effect on ASUD-75 than ASUD-99. In ASUD-75 samples, after ultrasound, a redistribution of the ratio of the intensities of valence vibrations of C=O bonds in the lactone (anhydride) group (1742 cm^{-1}) and the quinone (carboxyl) group (1683 cm^{-1}) is observed, which indicates the disintegration of the lactone ring and its transformation into carbonyl and carboxyl groups.

A more noticeable change in agglomeration for ASUD-75 compared to ASUD-99 under the influence of ultrasound can probably be associated with a change in oxygen groups on the surface of diamond nanoparticles.

Ultrasound of ASUD-75 samples leads to a significant increase in the intensity of the bands of O-H stretching vibrations (a broad band at the frequency of 3400 cm^{-1}) and symmetric and asymmetric stretching vibrations of the C-H bond (sp^3) (bands of 2890 and 2950 cm^{-1}), which means an increase in number of hydroxyl and phenolic groups. ASUD-99 have a hydroxyl group O-H (3400 cm^{-1}), which does not change significantly under the influence of ultrasound. The original ASUD-75 has weak responses from the hydroxyl group O-H (3400 cm^{-1}) and the phenolic group C-H (sp^3) (bands 2890 and 2950 cm^{-1}). But after the ultrasound treatment, they increase significantly, which indicates the removal of non-diamond carbon from the surface of ASUD-75 powders. All samples of ASUD-99 have a distinct peak at 3700 cm^{-1}. ASUD-75 does not have it. The isolated (free) OH- ion has only one degree of freedom, which corresponds to the frequency of the O-H valence vibration at about 3700 cm^{-1}. This explains the noticeable change in agglomeration for ASUD-75 in contrast to ASUD-99.



a

b

Fig. 4. IR spectra of ASUD-99 (*a*) and ASUD-75 (*b*) before (solid) and after ultrasonic treatment (dashed)

It is known that adsorption in mesopores depends not only on the adsorbent-adsorbate interaction, but also on the interaction between adsorbate molecules in a liquid adsorbed state, which leads to capillary condensation [5]. Ultrasonic treatment not only helps to clean the surface of powders by removing non-diamond carbon and impurities from the surface boundary of nanodiamond grains, it does not destroy carboxyl, anhydride, lactone groups. These groups significantly increase the hydrophilicity of the surface, which is associated with the formation of a hydrogen bond between water and these groups, which positively affects the process of adsorption of nanoparticles from aqueous solutions. The presence of mesopores in the studied samples, the size of which is 2÷50 nm, when in contact with liquids, significantly contributes to their volumetric filling and encapsulation of nanoparticles. Therefore, nanodiamond powders can be recommended as matrices for encapsulating nanoparticles from aqueous solutions. This opens up new opportunities for their practical use.

CONCLUSIONS

A large hysteresis is observed on the nitrogen adsorption isotherms of the initial samples of ACUD-75 and ASUD-99, which indicates the presence of mesopores in the porous structure. The volume of mesopores, defined as the difference between the total sorption volume and the volume of micropores, is 0.877 and 1.033 cm^3/g for ASUD-75 and ASUD-99, respectively. Thus, the investigated samples belong to mesoporous materials, their specific surface area, determined by the BET method, is characterized by close values and is 215 and 232 m^2/g, for ASUD-75 and ASUD-99, respectively, and a negligible content of micropores in the porous structure. Ultrasound of the samples of ASUD-75 and ASUD-99 does not affect the total sorption volume, and the values of the specific surface area of the studied samples do not change. It helps to clean the surface of the powders by removing non-diamond carbon and impurities from the surface boundary of the nanodiamond grain (with 0.4 and 0.32 % for

ACSD-99 and 0.67 and 0.55 % for ASUD-75) and reducing structural defects of the samples.

A more noticeable change in agglomeration for ASUD-75 compared to ASUD-99 under the influence of ultrasound is also associated with the formation of groups on the surface of diamond nanoparticles that change its hydrophilicity. Acidic groups predominate on the surface of UDA. In the samples of ASUD-75 after ultrasound, a redistribution of the ratio of the intensities of the valence vibrations of C=O bonds in the lactone (anhydride) group (1742 cm^{-1}) and the quinone (carboxyl) group (1683 cm^{-1}) is observed, which indicates the disintegration of the lactone ring and its transformation into carbonyl and carboxyl groups. It was found that all samples of ASUD-99 have a hydroxyl group O-H (3400 cm^{-1}), which does not significantly change under the influence of ultrasound.

The structural heterogeneity of the surface of ASUD-75 (the presence of carbon atoms in sp^2 hybridization) is due to the creation of a wider range of surface-containing oxygen groups grafted to different parts of the carbon matrix. Under the influence of ultrasound, they change. This explains the noticeable change in agglomeration for ACUD-75, in relation to ASUD-99. The presence of mesopores in the studied samples, the size of which is 2÷50 nm, when in contact with liquids significantly contributes to their volumetric filling and nanoparticle encapsulation. Therefore, nanodiamond powders can be recommended as matrices for encapsulating nanoparticles from aqueous solutions. This opens up new opportunities for practical use of ultra-dispersed detonation diamonds.

Вплив ультразвукової обробки на водні суспензії алмазних нанопорошків

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Встановлено, що ультразвукова обробка зразків алмазних нанопорошків сприяє очищенню поверхні за рахунок видалення неалмазного вуглецю та домішок з поверхневої межі зерна наноалмазів (з 0.4 та 0.32 % для АСУД-99 й 0.67 та 0.55 % для АСУД-75 відповідно). Вона не впливає на сумарний сорбційний об'єм і не змінює значення питомої поверхні досліджуваних зразків, але змінює склад груп на поверхні алмазних наночастинок, що впливають на їх гідрофільність.

У зразках АСУД-75 після ультразвукової обробки спостерігався перерозподіл співвідношення інтенсивностей смуг валентних коливань зв'язків C=O в лактонній (ангідридній) групі (1742 см$^{-1}$) та хіноновій (карбоксильній) групі (1683 см$^{-1}$), що свідчить про розпад лактонного кільця та його перетворення на карбонільну та карбоксильну групи. Усі зразки АСУД-99 мають гідроксильну групу O-H (3400 см$^{-1}$), яка суттєво не змінюється під впливом ультразвуку. Це пояснює помітну зміну агломерації для АСУД-75 на відміну від АСУД-99.

***Ключові слова**: алмазні нанопорошки, ультразвукова обробка, домішки, склад груп на поверхні, гідрофільність*

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