Effect of physicochemical action on the aggregative properties of detonation-synthesized nanodiamonds

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Abstract. The results of researches of physicochemical action on aggregate properties of nanodiamond are presented. The kinetics of aggregation of nanodiamond powder was studied as a function of time, temperature, and pH of the solution. The effect of the sp²–sp³ hybridization ratio of carbon in nanodiamond powders on their aggregation was studied. It is shown that the presence of non-diamond carbon in detonation synthesis nanodiamond powders leads to the increase of the mean diameters of particles, i.e., their agglomeration. The theoretical justification of the aggregation mechanism is proposed. It is shown that it is possible to control aggregative properties of nanodiamond powders by physicochemical influences, e.g., gas-phase thermal treatment to reduce the size of agglomerates and to create a well-developed reconstructed surface of diamond particles with a low content of functional groups on their surface.

1. Introduction

At present the world industry has aroused great interest in nanosized materials, especially in detonation-synthesized nanodiamond powders [1-3]. An essential obstruction in manufacturing various products based on nanodiamond powders is their high tendency to the aggregation, which is seen both in air and in liquid medium. The nanodiamond aggregation in liquid media is a complex physicochemical process. For the last ten years at the Bakul Institute for Superhard Materials physicochemical and surface properties of submicron and nanodisperse diamond powders of static and detonation syntheses are studied in detail. It was defined that physicochemical properties of nanodisperse diamond powders depend on the chemical composition of their surface and the nature of their functional groups [4-7]. Nanodiamond powders are characterized by an essential aggregation of grains, which does not allow steady suspensions to be prepared. The aggregation of nanodiamond particles consists of three basic stages [8, 9]: the integration of the initial particles, the formation of coarser aggregates from the initial particles, and the consolidation of aggregates through the redistribution of separate particles and initial aggregates under the action of viscous stress, which acts at the expense of the liquid medium. The aggregation of nanodiamond particles depends on the physicochemical properties of their surface. Physicochemical characteristics of the diamond functional cover are responsible for many diamond properties. In this case the portion of the surface atoms (Csurf) in the total amount of the carbon atoms, which is responsible for their contribution into the diamond properties, depends on the sizes of the diamond macromolecules. The contribution of the detonation-
synthesized nanosized diamond particles is especially high, according to the calculation, the weight of the functional groups is commensurable with the weight of a polycarbonic nucleus [9-11]. Any action on a diamond starts with the action on its functional cover; therefore the chemical state of the diamond surface may affect both the features of the action and the final result. The disordering of the surface layer may be considered as a structural effect of the surface strong deforming action on the neighbouring volumetric layers of a diamond. The main method to decrease the rate of the aggregation of nanodisperse diamond powders is a decrease of the amount of inclusions, in particular, metal and carbon, and the neutralization of energy charges of their surfaces [6, 8, 10]. As the powder dispersion increases, the aggregative and sedimentary stabilities increase. Accordingly, the free and interfacial energy increases, and according to the Gibbs–Helmholtz principle this energy in disperse systems tends to a spontaneous decrease. A decrease of the free interfacial energy occurs through a coagulation–coarsening of particles. Thus nanodiamond powders, whose single grain is 4–6 nm of size, in suspensions exhibit sizes from 3 to 20 μm. As it is known, in the real conditions suspensions of nanodiamond powders belong to thin suspensions, whose sizes are from 100 to 0.5 μm [6, 7]. The nature of a liquid phase, its viscosity, temperature, and pH value are the fundamental factors in the creation of stable suspensions. The prerequisite to the agglomeration of the nanodiamond powders is their chemical composition and adsorption properties. Therefore, the aim of our work was to study the effect of various physicochemical actions of the medium on the aggregative properties of the detonation-synthesized nanodiamond powders.

2. Methods of the investigations
The investigations were performed on nanodiamond powders of the following grades: ACUD80, ACUD90, ACUD95, and ACUD99 with the different contents of carbon phases (by the normative documents of Ukraine) in the initial state and with the reconstructed surface. Aggregative properties of nanodiamond powders have been evaluated by histograms of particle-size distribution. The histograms have been plotted by the instrumentality of a Seishin LMS-30 device. Mean diameter of nanodiamond agglomerates has been defined from the histogram data by special programs. In addition, aggregative properties of nanodiamond powders have been estimated by the rate of their sedimentation in solutions of different types. We studied the effects of the temperature, pH of the medium, contents of different forms of carbon, thermal gas-phase reconstruction of the surface on the diamond aggregative properties. The effects of the temperature and pH of suspensions on the aggregation kinetics of nanodiamond powders were studied on nanodiamond powders of the ACUD-99 grade at temperature from 25 to 75°C in solutions with pH from 3.5 to 8.9 for the time from 5 s to 1 h. Tested were 0.2% suspensions of nanodiamond powders in 1 l of distilled water with pH = 3.5 and in the solution of 9% sodium chloride with pH = 5.2 and pH = 8.9. The acidation of the suspensions of nanodiamond powders to pH = 3.5 was carried out by an addition of the solution of hydrochloric acid and the alakalization of suspensions of nanodiamond powders to pH of 8.9 was achieved by the addition of sodium hydroxide. A thermal gas-phase reconstruction of the surface was performed in two variants. According to the first variant (sample 1), samples of nanodiamond powder were annealed at 1000°C in the argon atmosphere and then cooled in argon. According to the second variant (sample 2), after the annealing of nanodiamond powders in the argon atmosphere at 1000°C the formed graphitized layer was oxidized by the air oxygen at 450°C [12]. The thermal gas-phase reconstruction of the surface was performed in two stages: annealing of nanodiamond powders at 1000°C in the argon atmosphere and then oxidation of the formed graphitized layer by air oxygen at 450°C. The rate of the nanodiamond particles aggregation during the deposition was defined by photometric method from a change of the suspension optical density and a change of the concentration of the nanodiamond particles in the suspension [13, 14]. For the first time by changing of optical density the stability of nanodiamond powders water suspension were evaluated. Thermal desorption spectra were taken using a MI 1201 mass-spectrometer in the temperature interval 20–600°C. Adsorption-structural and physicochemical studies of the powders surfaces were carried out by the classical method of the gas adsorption at lower temperatures in concordance with the BET principle.
using a NOVA 2200 gas-adsorption analyzer (Quantachrome, USA), which are intend for the measurement of the porosity, surface specific area, radii of pores, etc. The principle of operation is a static manometric method. Studies of the metal ions adsorption process on the diamond surface were performed using the photocolorimetric method from solutions of same-named salts in concentrations of 1:10.

3. Results and discussion

The nature of the liquid phase, its viscosity, pH values and temperature are fundamental factors at the creation of stable suspensions. In figure 1 the kinetics of the change of the ASUD 99 nanodiamond powders sedimentation rate in time is shown, and in figure 2 the variations of the sedimentation rate of nanodiamond powders vs. pH of solutions.

![Figure 1](image1.jpg)  ![Figure 2](image2.jpg)

**Figure 1.** Dependence of the sedimentation rate of the ASUD 99 nanodiamond powder in distilled water on the temperature and exposure time: T = 25°C (curve 1), T = 50°C (curve 2), T = 75°C (curve 3).

**Figure 2.** Dependence of the sedimentation rate of the ASUD 99 nanodiamond powder on pH of a solution (suspension) and exposure time: pH = 8.9 (curve 1), pH = 6.5 (curve 2), pH = 3.5 (curve 3).

It follows from figure 1 that for the first ten seconds of the deposition of diamond particles aggregates a rectilinear section is observed that characterizes a decrease in the sedimentation rate of diamond particles. After the first 10 s the sedimentation rate decreases and after 70 s becomes virtually constant, i.e., the process of aggregation is completed for 70 s.

In studying the effect of heating the suspensions of nanodiamond powders in distilled water at temperatures from 25 to 55°C, and 75°C on the aggregation kinetics of nanodiamond particles (figure 1), it was found that with increasing temperature of a suspension of nanodiamond powders in a distilled water the concentration of particles in the interval under study decreases, i.e., with increasing temperature the aggregation rate increases.

The aggregation rate of nanodiamond powders depends on the pH of the suspension solution. The aggregation kinetics of nanodiamond powders in solutions based on distilled water at the room temperature at different pH values of the solution is given in figure 2. It is seen that as the pH value of the solution increases, the concentration of diamond particles in the suspension in the interval under study increases, thus decreasing the sedimentation rate, i.e., in the alkaline medium the aggregation process becomes slower. Thus, the alkalization of suspensions essentially reduces the sedimentation rate of nanodiamond particles.

Of interest was to compare the change of the mean diameter of particles of nanodiamond powders of different grades with the change of the carbon phase concentration. The following grades of nanodiamond powders were studied: ASUD 80, ASUD 90, ASUD 95, ASUD 99, which differed by the fixed relation of carbon phases of the sp²- and sp³-hybridization.
The table 1 gives the basic adsorption-and-structural characteristics of ASUD 99 nanodiamond powders after the two-staged gas-phase reconstruction of the surface.

**Table 1.** Physicochemical properties of the surfaces of the initial and reconstructed ASUD 99 powders.

| Characteristic                  | ASUD 99 init. | Sample 1 | Sample 2 |
|--------------------------------|---------------|----------|----------|
| Specific surface area \( S_{\text{BET}} \), \( \text{m}^2/\text{g} \) | 242           | 245.0    | 256.4    |
| Pore volume, \( V \), ml/g     | 1.045         | 1.0      | 1.816    |
| Mean radius of pores, \( R \), Å | 86            | 80.0     | 141      |
| Mean diameter of particles, \( d_{\text{mean}}, \mu\text{m} \) | 12.6          | 2.28     | 4.764    |
| Adsorption potential, \( \Lambda \), J/g   | 12.2          | 12       | 14       |
| Parameter \( K \), %            | 12.6          | 12       | 10       |

In our studies it was defined that with increasing concentration of non-diamond carbon in nanodiamond powders the mean diameter of particles increases, thus indicating the intensification of the aggregation process (figure 3).

**Figure 3.** Dependence of the change of the particles mean diameter of the nanodiamond powder on the concentration of non-diamond carbon

Based on the data obtained the following mechanism of the aggregation is proposed. The mechanism implies that the aggregation is realized in several stages:

– adsorption of oxygen-containing groups from solutions and thus formation a functional cover;
– establishing the equilibrium between the solution and functional cover, agglomeration through the Van der Waals forces;
– agglomeration through covalent (chemical) forces.

The nanodiamond powder is characterized by a polycrystalline structure. The nanodiamond particle consists of a nucleus, a shell of non-diamond carbon and functional groups of different composition. As a rule, agglomerates of nanodiamond powders consist of several diamond clusters, in which the bond between diamond nuclei is realized with the help of functional groups [4, 15].

It follows from the above that in many cases oxygen-containing groups are responsible for aggregation properties of powders. Because of this we studied the influence of the thermal gas-phase reconstruction on a changing the functional cover and on aggregative properties of nanodiamond powders. It was defined that the samples of nanodiamond powders subjected to the thermal annealing at 1000°C in the argon atmosphere and cooled in the same atmosphere (sample 1) exhibited the minimum size of agglomerates – 2.8 \( \mu \text{m} \). Obviously, the annealing of powders at 1000°C and cooling them in the argon atmosphere made it possible to clear the surface from oxygen-containing groups, graphitize the powder surface, and reduce the aggregation rate. The oxidation of powders by the air
oxygen (sample 2) allowed us to remove a graphitized layer of nanodiamond powder, but at the same time new oxygen-containing compounds appeared on the surface and the mean diameter of nanodiamond powders increased by a factor of 2. The mean diameter of the agglomerates are presented in the table 1.

It follows from the data given in the table that after a two-stage gas–phase reconstruction of the surface of nanodiamons powder according to the described above scheme, the specific surface of powders (sample 2) and the adsorption potential of them somewhat increased (no more than by 10%), but at the same time the volume of pores increased considerably by a factor of 1.7.

Figure 4 shows the IR spectra of the initial and after thermal gas-phase reconstruction of nanodiamond powders were recorded in the near and middle infrared range on the Nexus IR Fourier spectrometer. The broad band at 3410 cm\(^{-1}\) corresponds to valence O-H vibrations of absorbed water on the surface (or N-H oscillations). Peaks 2890 and 2950 cm\(^{-1}\) are symmetrical and asymmetric valence vibrations C-H. Peak 1750 cm\(^{-1}\) corresponds to valence C=O vibrations in the carbonyl and carboxyl groups, 1635 cm\(^{-1}\) responds to the deformation O-H vibration (or / and N-H and C-N valence vibrations).

In the frequency range 1000-1500 cm\(^{-1}\) there is a large number of bands (with a complex contour), among which the main interest connected with 1380 cm\(^{-1}\) peak of low intensity (a small component compared to others) corresponds to the N-O valence vibration of NO\(_x\) groups (a consequence of treatment with nitric acid), or corresponds to OH vibrations in the COOH group. Peak 1260 cm\(^{-1}\) is associated with C-N vibrations. Superposition of bands in the range 1000-1200 cm\(^{-1}\) correspond to C-O vibrations =C–O–C= groups. Wide bands with a low signal-to-noise ratio in the range 1900-2700 cm\(^{-1}\) are artifacts (absorption of the diamond element of the apparatus), which arose when measured by the method of fully deformed total reflection.

![Figure 4](image.png)

**Figure 4.** IR spectra of initial nanodiamond powders (1) and after gas-phase treatment (2).

IR-spectrum of sample 2 (table 1) after thermal gas-phase reconstruction (curve 2) in comparison with the spectrum of the initial sample (curve 1) contains bands at the frequency range 1000-1750 cm\(^{-1}\) of significantly lower intensity, what means a lower content of carbonyl and carboxyl groups.

Thermodesorption spectra (figure 5) of vapors, carbon monoxide and dioxide for the initial nanodiamonds and after the gas-phase reconstruction of the surface (for sample 2 in table 1) verify that on the surface of nanodiamond powders with the reconstructed surface (curve 2) the amount of physical and chemical adsorbed vapors is much below than on the initial surface, the content of CO is insignificant, and CO\(_2\) is absent. These studies confirm the obtaining of nanodiamond powders surface, which is purer from functional groups.
Thus, it is shown that, by physicochemical influences, it is possible to control the aggregative properties of nanodiamond powders, for example by gas-phase heat treatment, to reduce the size of agglomerates and to create an elaborate reconstructed surface of diamond particles with a low content of functional groups on their surface.

It was of interest to study the sedimentation stability of produced nanodiamond powders treated according to two-stage gas-phase treatment. From the ASUD 99 nanodiamond powders (sample 2) a water suspension with the concentration 0.64% and volume of 250 ml was prepared.

The sedimentation stability of this suspension with time was studied. The suspension was stable for 3 months. In this case the optimal density of the suspension \( D = 5.5 \, \text{B} \) was kept for all the period of time. The distribution of agglomerates of diamond particles and their mean diameter was defined in the finished suspension. The mean diameter of agglomerates in a finished suspension was 0.403 \( \mu \text{m} \).

We studied adsorption properties of a nanodiamond powder with a reconstructed surface relative to chromium ions (VI) [16].

The efficiency of the heavy metal ions recovery from the modal solution exceeds 70%, the kinetic parameters of the process are defined. It has been established that nanodiamonds rapidly and efficiently recover chromium ions (VI) at the static conditions: for first 5 min the concentration of them decreases more than by 50%.

Based on our investigations, a novel composite filter material on the base of basalt, lavsan, and cellulose fibers with the addition of detonation-synthesized diamond nanopowder for purification of water from heavy metals ions was developed. The testing of the developed material after additional (final) drains after the treatment of the synthesis product during the diamond recovery shows that the drains correspond to the maximum permissible values for a drinking water.

4. Conclusions
1. The kinetics of aggregation of nanodiamond powder depending on time, temperature, and pH solution was studied. It has been established that the aggregation rate of the freshly made solution is so much large that the aggregation of almost 90% of nanodiamond powder occurs for 10 s. With the temperature increase the aggregation rate also increases. It was defined that the alakalization of the solution results in a decrease of the aggregation rate because due to the dissociation of oxygen-containing compounds of the surface layer.

2. The effect of the ratio of the sp\(^2\)–sp\(^3\) hybridization of carbon in nanodiamond powders on their aggregation was studied. It is shown that the presence of non-diamond carbon in nanodiamond powders of detonation synthesis leads to the increase of the mean diameters of particles, i.e., their agglomeration.

3. The theoretical justification is proposed of the aggregation mechanism, which implies that the aggregation process takes place in several stages that include the adsorption of oxygen-containing groups from the solution and thus formation of the functional cover; establishing of the equilibrium
between the solution and agglomeration functional cover through Van der Waals forces; agglomeration due to covalent (chemical) forces.

4. The possibility is shown to control aggregative properties of nanodiamond powders by physicochemical actions, e.g., gas-phase thermal treatment to decrease agglomerates and create well-developed reconstructed surface of diamond particles with a low content of functional groups on their surface.

5. The use of nanodiamonds having the developed surface ensures the producing a stable suspensions.

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