The growth of agglomerates in the conditions of detonation synthesis of diamond

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Abstract. The conditions of detonation synthesis of nanodiamonds do not affect the size of diamond microcrystallites too much, as was shown in numerous experimental studies. This is because microcrystallites are formed almost instantly at the moment of explosive detonation, when conditions are created for crystallization of the diamond carbon phase. Further expansion of detonation products only leads to the creation and enlargement of particle agglomerates. The product of detonation synthesis is always a powder consisting of agglomerates of carbon particles of diamond and non-diamond phases with impurities. The size, density and specific surface area of the agglomerates can be different depending on the synthesis conditions. These product characteristics are of great importance for further technological applications. Meanwhile, the processes of agglomerate formation under conditions of expansion of detonation products have not yet been considered. In this paper, we theoretically consider this process. The dependences of the size and specific surface of carbon agglomerates on the conditions of detonation synthesis were obtained, and comparison with experimental data was made.

1. Introduction

Despite the fact that the technology of detonation synthesis of nanodiamonds has existed for decades, there is still no understanding of all the processes occurring in the explosive chamber. It was not possible to achieve a significant increase in the size of microcrystallites of nanodiamonds. The particle size of the diamond phase is from 3 to 9 nm [1]. Despite the obvious uniqueness of the physicochemical properties of the obtained material and the relative cheapness of the synthesis technology, insufficient application fields have been found so far. Therefore, further studies of detonation nanodiamonds (DND) are carried out aimed at studying the fundamental processes of its synthesis and identifying new areas of use. The study of the mechanism of DND synthesis seems to be most important, since its knowledge is necessary both for improving production technologies and for managing the structural state of the resulting product.

The detonation synthesis product is a powder consisting of highly porous nanostructured agglomerates of particles of various carbon phases with metallic and nonmetallic impurities. Carbon powder has a multi-level hierarchical structure: porous flakes are composed of agglomerates of particles composed of smaller agglomerates. At the lower level of the hierarchy are diamond single crystals with mechanical contacts between them and their monolithic intergrowths [2, 3].

After obtaining, the product is purified. Depending on the cleaning technology, the resulting product properties change. The impurities contained in the diamond after refining have been identified...
and studied [4,5]. The cleaning technology affects not only the fraction of the diamond phase in the powder, the composition and amount of impurities, but also the size of the agglomerates and their specific surface [6]. Cleaning also increases the cost of the resulting product.

On the other hand, the crude powder obtained as a result of detonation synthesis is in itself a valuable technological product. Its value depends primarily on the size and structure of agglomerates. Meanwhile, in the literature there is no description of the mechanisms and patterns of the formation of particle agglomerates in the process of detonation synthesis. One of the reasons hindering the industrial use of DND is the insufficient study of the relationship between the quality of DND powder and the conditions for its synthesis, in particular, the degree of particle connectivity to agglomerates [6]. It was experimentally established that due to changes in the synthesis conditions, the sizes of the resulting agglomerates can vary from 10 nm to 100 μm, and the specific surface of the particles can vary from 20 to 500 m²/g. It was experimentally found that the composition and structure of DND agglomerates are affected by increased coagulation time due to the mass of the charge and the massive shell around the charge; temperature, pressure; carbon concentration in detonation products.

The purpose of this work is to provide a mathematical description of the processes of formation of agglomerates of carbon particles during detonation synthesis of nanodiamonds and to carry out calculations using this description. Such calculations will help to make suggestions on the synthesis conditions in order to obtain a powder with specified dimensional properties.

2. Mathematical model of coagulation of carbon particles in the detonation synthesis of nanodiamonds

Suppose that at the time of the explosion, “primary” carbon particles of a diamond and graphite phase of nanometer size instantly form. In the process of expansion of detonation products, the conditions for further growth of diamond crystals disappear, but there are conditions for coagulation of the formed particles into more or less strong porous and large agglomerates.

The growth of agglomerates under conditions of detonation is a complex process, depending on various parameters. Moreover, it can hardly be described in the framework of the Brownian model of coagulation. Obviously, the process speed is affected by the features of unsteady turbulent flows during expansion of detonation products. In addition, under conditions of detonation synthesis, pressure oscillations with a frequency of about 1÷10 kHz occur in the explosive chamber [7], caused by reflection from the walls and degeneration of the shock wave. These factors significantly accelerate the coagulation of particles. In [8, 9], an expression was obtained for the relative mean volume as a function of time \( t \) under shear isotropic turbulent flow:

\[
V = \exp\left(A \frac{\varepsilon}{\sqrt{\nu} n_0 t}\right),
\]

where \( \varepsilon \) is the local energy dissipation rate, \( \nu \) is the kinematic viscosity of the detonation products, \( r_0 \) is the initial particle radius, \( n_0 \) is their initial concentration, constant \( A = 2.6 \). Assuming the sphericity of the primary particles, we have \( r_0 n_0 = \frac{3}{4\pi} \frac{w}{\rho} \), where \( w \) is the mass of carbon in detonation products, \( \rho \) is the density of carbon particles. The approximate estimates obtained in [10] give the magnitude of the particle growth time to sizes of 200 nm as \( t \sim 3 \cdot 10^6 \) s. However, these are approximate estimates that do not take into account differences in particle sizes, a change in the concentration of the evolution of the particle size distribution. We obtain a more accurate solution to the problem of coagulation of carbon particles based on the Smoluchowski evolutionary model. Suppose that each collision of particles leads to their adhesion (in the more general case, a certain fraction of collisions leads to adhesion; this fraction can serve as one of the model parameters).

The mass function of the particle size distribution is determined from the solution of the Smoluchowski balance equation [11]:

\[
\frac{\partial g(r,t)}{\partial t} = I_1 + I_2,
\]

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where $I_1$ describes the loss of particles with a radius $r$ per unit time in a unit volume due to the collision of a particle of radius $r$ with a particle of radius $r_1$:

$$I_1 = -g(r,t) \int_0^\infty K(r,r)g(r_1,t)dr_1.$$  \hfill (3)

$I_2$ describes the appearance of particles of radius $r$ due to the collision of particles with radius $r_1$ and $r - r_1$:

$$I_2 = \frac{1}{2} \int_0^\infty K(r-r_1,r_1)g(r_1,t)g(r-r_1,t)dr_1.$$ \hfill (4)

The initial conditions for the system of equations (1-3): $g(r,t_0) = g_0(r)$ is initial particle size distribution. Since nanodiamond particles are formed immediately at the moment of the explosion, and then only agglomerate, the nanocrystallite size does not change and can be determined by X-ray diffraction analysis in detonation synthesis products.

The higher the probability of particle collisions, the faster coagulation will occur. In the absence of any effect, this quantity is determined by the Brownian motion. In model (1-4), the probability of collisions of aerosol particles under conditions of Brownian coagulation was considered proportional to the sum of squares of particle diameters:

$$K(r,r_1) = k_b r^3 + r_1^3,$$ \hfill (5)

where $k_b$ is the coefficient of proportionality \([\text{m}^2/\text{s}^2]\) (Brownian coagulation).

In the case of turbulent coagulation, taking into account (1), the expression for the kernel of the integral equation takes the form:

$$K(r,r_1) = k_t \sqrt{\frac{\epsilon}{\nu}} r^3,$$ \hfill (6)

where $k_t$ is the coefficient of proportionality (turbulent coagulation).

The kernel of the integral equation $K(r,r_1)$ has the meaning of the probability of particle collisions and has a dimension of $1/\text{s}$. The probability of particle collisions during Brownian coagulation is obviously less than in a turbulent flow, since the collisions are random in nature. In a turbulent flow, vortices lead to turbulent mixing and intense collision of particles. In both cases, the probability of collisions is proportional to the concentration and volume of the particles. With Brownian coagulation, the movement of particles is slower, the higher the viscosity of the medium, which is included in the denominator of equations (5) for Brownian coagulation. In turbulent coagulation, an important parameter is the ratio of the energy dissipation rate to the dynamic viscosity coefficient.

Coagulation time depends on the synthesis conditions: explosive charge mass, explosive chamber dimensions. Particles coagulate until deposition on the walls of the chamber. This time can be obtained from solving the problem of expanding detonation products and experiments using the T-20 method [12]. So, for example, for HMX, the expansion rate of detonation products is $1.6\div1.8 \text{ km/s}$. Then the coagulation time can be estimated as $t_c \sim L/W$, where $L$ is the characteristic size of the explosive chamber.

Taking in equation (2) as the characteristic scales $t_c$ for time, $r_{mean0}^3$ (initial value of the average particle radius) for the particle radius, we can distinguish a dimensionless complex characterizing the process:

$$\overline{K} = k_t \sqrt{\frac{\epsilon}{\nu}} r_{mean0}^3 t_c.$$ \hfill (7)

Solving equation (2) in dimensionless form, we obtain the dependence of the relative mean particle radius $r_{mean} = r_{mean}/r_{mean0}$ on dimensionless time $\theta = t/t_c$. As the mean radius, we take $r_{mean0} = d_{32}/2$, where $d_{32}$ is the Sauter diameter. As the initial particle size distribution, we choose the normal
distribution. Then the mathematical expectation $\mu$ of the distribution of the dimensionless particle radius will be equal to unity. The dimensionless process time will vary from 0 to 1.

3. Results and discussion
As a result of coagulation, the particle size spectrum shifts toward larger ones due to the appearance of “waves” of larger particles. Sauter diameter also grows, and the stronger, the larger the parameter $\bar{K}$ (figure 1). The calculation is made for $\bar{K} = 0.5$. Figure 2 shows the change in the relative particle radius with time for different values of the parameter $\bar{K}$.

![Figure 1](image1.png)

**Figure 1.** Mass distribution of particles by relative sizes at zero time and at time $\theta = 1$ (end of expansion of detonation products).

![Figure 2](image2.png)

**Figure 2.** Dependence of the relative mean particle radius on the dimensionless process time.
A noticeable (tens and hundreds of times) increase in particle sizes corresponds to the condition $K \gg 1$. In the experiment, there is an increase in particle agglomerates from $\sim 5 \text{ nm}$ to $\sim 1\div10 \mu\text{m}$, that is, 1000 times or more.

The calculations showed that the dependence of the increase in particle size on the parameter $\bar{K}$ is linear, with the parameters:

$$r = a \bar{K} + 1,$$

where $a \sim 91$. In dimensional variables, equation (10) takes the form:

$$r_{\text{mean}} = r_{\text{mean}0} + a \bar{K} \sqrt[4]{\rho_0 \tau_{\text{mean}}^4 L^4}.$$

It follows from equation (9) that the larger the concentration of particles, the longer the expansion time of detonation products (proportional to the size of the chamber), the larger the initial particle size, the larger the final size of the agglomerates. However, equation (9) gives a weaker (linear) dependence of the growth of agglomerates on time than the estimated equation (1). An exponential increase in the volume of agglomerates over time is hardly true, since in this case a significant (multiple) spread in particle sizes would be known in different experiments, which is not observed.

Analyzing equation (9), we can conclude that the size of the agglomerates is proportional to:

- the expansion time of the detonation products $\tau_e \sim L / W$;
- the size of the primary nanocrystallites in the fourth degree;
- the concentration of particles in the detonation products: $n_0 \sim M_e / L^3$;
- the ratio of local energy dissipation in a turbulent flow to the value of the dynamic viscosity of detonation products.

Note that the final size of the agglomerates is proportional to the product of particle concentration by the process time: $n_0 \tau_e \sim M_e / (L^2 W)$. This means that an increase in the size of the explosive chamber with the same charge weight will, according to the model, lead to a final reduction in the size of the agglomerates, in proportion to the square of the characteristic size of the chamber. An increase in charge mass with the same chamber size will lead to an increase in the size of agglomerates and, accordingly, to a decrease in the specific surface area of the powder.

Let us consider the results of experimental studies of detonation synthesis nanodiamonds obtained under industrial conditions by detonation of charges of TNT with hexogen (TH) and hexogen with graphite (HGr). The synthesis involved charges of different weights: from 0.5 to 2 kg. The sizes of diamond single crystals were experimentally estimated using X-ray diffraction analysis. They amounted to 4.7÷5.2 nm in a series of experiments with a charge of HGr and 3.3÷3.6 nm with a charge of TH. The specific surface area of the obtained particles (agglomerates) was measured by the BET method. In the calculations, the size of the single crystal, experimentally measured in each synthesis variant, was taken as $r_{\text{mean}0}$. Using the equation (11), the radius value of the resulting agglomerate $r_{\text{mean}}$ was calculated, and then the specific surface area of diamond particles with a radius $r_{\text{mean}}$ was calculated. The obtained dependences on the mass of the charge are shown in figure 3.
Figure 3. Dependence of the specific surface area of detonation synthesis nanodiamond agglomerates on the charge mass of TH and HGr.

The correlation between the experimental and calculated values of the specific surface is 99%, which indicates the adequacy of the proposed model, at least in terms of the dependence of the size of the agglomerates on the mass of the charge.

The trend of a decrease in the specific surface area of particles with increasing charge mass was noted in [1]. In the experimental results presented there, the charge mass increased from 0.1 to 140 kg. The size of diamond nanoparticles was 3.5÷5 nm, and the specific surface area of the particles decreased from 310.4 to 181.2 cm² / g for charges weighing 0.1 and 140 kg, respectively.

4. Conclusions
A mathematical model of the coagulation formation of nanodiamond agglomerates under conditions of detonation synthesis is proposed. Based on the analysis of published data, it was concluded that diamond nanocrystals are formed almost instantly at the moment of detonation. Further growth of agglomerates occurs due to coagulation of carbon nanoparticles with an increase in size by hundreds and thousands of times.

The mathematical model is based on the analysis of the integral balance equations of Smoluchowski taking into account the peculiarities of coagulation in a turbulent flow. As a result of the numerical parametric analysis of the model, we obtained simple patterns that allow us to draw conclusions about the possibility of controlling the agglomeration of carbon particles in the conditions of detonation synthesis of nanodiamonds. The process parameters that can be controlled are the size of the detonation chamber, the mass of the charge, the size of the primary diamond nanocrystallite. Depending on the values of these parameters, larger or smaller sizes of agglomerates can be obtained. In this case, an increase in the characteristic size of the detonation chamber (proportional to the square of the linear size) and a decrease in the mass of the explosive charge will lead to a decrease in the size of the agglomerates, and an increase in the mean size of the primary diamond nanocrystallites will increase the size of the agglomerates in proportion to the fourth power of the size of the nanoparticles.

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