Physical–chemical model of processes at detonation synthesis of nanodiamonds

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Abstract

This article presents a principally new physical–chemical model of nanodiamond formation at explosion, which describes adequately all the existing experimental data on detonation synthesis of diamonds. According to this model, the detonation wave performs activation rapidly; then the reaction mixture composition keeps varying. In the diagram $C – H – O$ this process results in continual motion of the point imaging the reaction mixture composition. The ratio of the diamond phase amount to the condensed carbon quantity in the explosion products is defined by the width of the section this point passes over in the diamond formation zone. Motion of the point in the area below the line $H – CO$ results in decrease of the condensed carbon (CC) amount. Diamonds are formed by the free-radical mechanism in the unloading wave. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Methods of diamond formation can be divided tentatively into two groups. The first group comprises the methods involving the phase transition graphite $\rightarrow$ diamond. Graphite turns diamond at high temperature and pressure. The second group consists of the methods of chemical formation of diamond films. They arise on a substrate due to chemical reactions proceeding in plasma. In so doing, temperature can be below 1000 K and pressure can be 1 kPa to 0.1 MPa. Till now, the detonation method of diamond formation was referred to the first group, since ultra fine diamonds were considered to arise directly in the detonation wave (Fig. 1, the section bc), i.e. from free carbon at a temperature of 2000 – 3500 K and a pressure of 10 – 30 GPa. However, \textit{in situ} investigation of the dynamics of nanodiamond formation performed in work [1] has demonstrated that UFD are formed in 500 ns after the shock wave (SW) front passage, beyond the detonation wave. Hence, the detonation wave (DW) just creates the reaction mixture (plasma), from which then diamonds are formed in the course of chemical reactions. That is why detonation synthesis of UFD should be referred to the second group.

2. Physical–chemical model

Conductivity of detonating high explosives (HE) has been presented in many works (e.g. see [1,2]). Dependence of conductivity on time can be described in terms of hot spots in the following way. After the shock wave (SW) front passage, conductivity is observed growing monotonously for approximately 100 to 200 ns [1,2]. That may relate to the initial stage of detonation: from formation of centers of explosive destruction — hot spots (HSs) directly beyond the SW front — to involving most of the explosive in the chemical reaction. At this stage, temperature and pressure keep growing continuously (Fig. 1, the section abc), reaching their maximal values in 100 to 200 ns. According to the data in work [1], the relative change of specific volume of matter in the detonation region in the first 100 ns is less than 5%. The reaction zone is expanding continuously and new products of destruction of the explosive keep arriving there. Intense heating of
the products of destruction results in formation of a low-temperature high-density plasma [2].

The triangle diagram $C - H - O$ turned out to be very useful in selecting a carbonic gaseous mixture to make diamond films by the CVD method [4]. It was found empirically that diamond films grow only at compounds corresponding to a relatively narrow band along the line $H - CO$. Since the CVD method implies usage of flow reactors, composition of reactants does not change with time. Any reaction mixture undergoes continuous activation (thermal, microwave etc.) for production of free radicals. It has been shown for the CVD method [4–6] that, irrespective of composition of the gaseous mixture fed to the reaction zone and on the reactor structure, diamond films can grow if plasma composition in the diagram $C - H - O$ corresponds to a narrow zone above the $H - CO$ line (see Fig. 2). Thus, diamond formation does not depend on the character of components fed to the reaction chamber because they disintegrate rapidly and efficiently into small molecules, radicals or ions.

As it has been shown by experiment [1], UFD synthesis as such is preceded by a detonation wave. That is why in this physical–chemical model we suppose that at detonation diamond a detonation wave activates synthesis in a short time (300 to 500 ns). While in the CVD method flow reactors are used and composition of reactants is stationary near the growing diamond film, the reaction mixture composition is continuously changing in the course of detonation synthesis. In 200 ns, no more new products of destruction are coming to the reaction space and comminution of reactant molecules is completed. Since oxygen partially leaves the reaction mixture in the form of explosion products ($H_2O$, $CO_2$, $CO$, etc.), the ratio $[C]/([C]+[O])$ grows. In the triangle diagram $C - H - O$ this process results in a continuous motion of the image point to the area with increasing relative amount of carbon in the reaction zone. For explosives of the $C_aH_bN_cO_d$ type, the quantitative composition of plasma is defined by the chemical composition of the explosive. However, the qualitative composition of plasma changes only if the coefficient $b$ or $d$ equals zero. If not, it remains practically the same. It is rather difficult to compare quantitatively the output of UFD detonation synthesis obtained by different scientific groups since it depends not only on the HE composition but also on the conditions of cooling of the diamonds formed (e.g. see [7]). However, these results can be compared qualitatively in terms of our model. For most HEs used for detonation synthesis of diamonds [3,8,9], the concentration ratio $[C]/[O]$ is less than 1 and is depicted in the diagram $C - H - O$ by points below the line $H - CO$, in the area where no diamonds arise. For trinitrotoluene (TNT): $[C]/([C]+[O]) \approx 0.54$ and $[H]/([H]+[C]) \approx 0.42$ (see Table 1). The corresponding point in the triple diagram lies in the diamond zone near the boundaries with the region where condensed carbon arises in its non-diamond forms (Fig. 2). In the course of reaction, the relative content of carbon increases and the reaction mixture moves rapidly into the zone where non-diamond carbon is formed. That is why the relative content of nanodiamonds in the condensed carbon (CC) (UFD/CC≈15.7%) is almost 5 times less

<table>
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<th>Explosives</th>
<th>UFD/HE %</th>
<th>CC/HE %</th>
<th>UFD/CC %</th>
<th>$\frac{[C]}{[C]+[O]}$</th>
<th>$\frac{[H]}{[H]+[C]}$</th>
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![Fig. 1. The schematic of detonation wave.](image1)

![Fig. 2. The triangular diagram.](image2)
than after explosion of the following composition: trotyl — 60%, hexogen — 40% (UFD/CC=72.7%) (hereinafter data on UFD and CC content have been taken from [3]). For such explosive composition we have \([C]/(\{C\}+\{O\}) \approx 0.47\) and \([H]/(\{H\}+\{O\}) \approx 0.5\). This point is below the diamond formation zone, that is why the CC amount is not maximal and the relative content of UFD in the CC equals 72.7%. The latter is caused by the fact that the line plotted by the reaction mixture composition passes through the diamond zone in its widest part. In a trinitroresorcinol/hexogen system (20/80%), the carbon content in the initial stage process. Atomic hydrogen decomposes long hydrocarbon molecules into shorter fragments, which prevents polymerization and formation of cyclic compounds, whose deposition on the surface of diamonds would hinder them from further growth. Hydrogen interacts with neutral molecules, e.g. methane, which leads to formation of free radicals providing diamond particle growth. During this radical reaction the growing nanodiamond has a surface layer of hydrocarbon radicals. This is the main mechanism of diamond film growth. The main principle of chemical synthesis of nanodiamonds is the necessity of creating a chemical process maintaining \(sp^3\) hybridization. Since the diamond phase is metastable, formation of its germs is hindered (low temperature and pressure) and the substrate surface is subjected to coating with a “seed” layer of diamonds or scratching with other diamonds (or some similar methods are used).

At detonation diamond synthesis, the detonation wave forms a reaction mixture similar to that used in the CVD method. The synthesis is performed at high temperatures and pressures in the region of stable diamond phase. Thus, rapid rise and growth of a new phase takes submicroseconds. Experiments with atoms of isotopes have shown that UFD are characterized by a higher content of carbon of the methyl group of TNT molecule. On the surface of diamond particles, including those obtained from a mixture of hexogen and soot by the detonation wave method, there was found, besides functional oxygen-containing groups, a large amount of saturated hydrocarbon radicals [9,10]. Therefore, thin diamond film and UFD are formed by the same chemical mechanism. In the course of radical reaction, a growing nanodiamond has a surface layer consisting of hydrocarbon radicals. The growing diamond cluster surface absorbs, besides hydrocarbons and atomic hydrogen, other free radicals and molecules existing in the reaction mixture volume: \(CO, H_2, N_2\), etc., which is partly confirmed by element analysis and IR spectroscopy [9]. Thus a detonation diamond is formed in the course of chemical reactions proceeding in the rarefaction region. Another way to produce diamonds is the following process: \(\text{Olefins} \rightarrow \text{Carbon} \rightarrow \text{Diamond}\). Here free carbon (in the form of soot, graphite and so on) is formed from olefins. However, it has been shown experimentally and theoretically that the rate of diamond formation from graphite lowers with increase in pressure. Really, the logarithm of the kinetic constant depends on the pressure in the following way [11]:

\[
\ln r = \text{const} - \frac{\Delta v^g \cdot p}{kT},
\]

where \(k\) is the Boltzmann constant and \(\Delta v^g\) is the difference between the atomic volume of activated complex that of graphite. Whereas \(\Delta v^g > 0\), diamond formation rate decreases significantly with pressure growth.

This process does not occur at detonation synthesis because the typical time of reaction is insufficient for the carbon phase to turn into the diamond one. Addition of graphite or soot to the initial HE allows realization of the following transformation:

\(\text{Graphite, Soot} \rightarrow \text{Diamond}\).

Work [12] used the isotope method to investigate the detonation synthesis of diamonds from a mixture of HE (hexogen) with a carbon addition (soot). It has revealed that...
the whole fraction of UFD in the arising diamond phase consists of carbon atoms of hexogen. Within the framework of our chemical–physical model that means that a phase transition by scheme Graphite, Soot → Diamond is attended by synthesis of UFD from free radicals by the scheme Alkyls (and other free radicals $C_xH_y$) → Diamond.

The order of magnitude of detonation diamond growth rate $G$ can be estimated as the ratio of the average nanodiamond diameter to the time of escape of nanodiamonds from the reaction volume ($t_r$). From the data of work [1], the average diameter of diamond particles is 50 Å and $t_r$ equals 0.5 µs, whence we obtain $G = 0.01$ m/s. The rate of diamond film growth at a pressure of 100 mm mercury is approximately $10^{-8}$ m/s. The cause of the ~$10^5$-fold increase of the diamond film growth rate is that pressure in the UFD formation zone is also approximately $10^6$ times larger. The rate of UFD and diamond film growth should be of the first order with respect to hydrocarbon radical concentration in the region adjacent to the growing cluster surface. Correspondingly, at detonation diamond synthesis, the reaction mixture density is also $10^6$ times larger than at growing diamond films on substrates of different materials. Let us consider the diffusion mechanism of diamond formation. For this purpose we will estimate the diffusion constant required for growth rate $G$. Using the Einstein formula we immediately have the following estimate: $D \sim d^2 / t_r \sim 10^{-15}$ m$^2$/s. Characteristic orders of diffusion constants are $\sim 10^{-5}$ m$^2$/s in gases, $10^{-9}$ m$^2$/s in liquids (weakly depending on temperature in both cases) and $10^{-12}$ m$^2$/s in solids at temperatures close to the melting point and much less at lower temperatures. So, UFD can grow by diffusion mechanism both in liquid and gaseous media. Properties of the medium where detonation UFD are formed are typical of a liquid state. In spite of high concentration of radicals, the rate of their recombination $r_{rec}$ is much less than that of their joining to diamond nanoparticles. Since diamond particles are small ($\sim 50$ Å) and have a relatively big mass (up to 10% from the mass of the explosive), their concentration is approximately $10^{25}$ m$^{-3}$. The average distance between clusters is approximately 100 Å. Nanoparticles have big specific surface, $S \sim 10^7$ m$^{-1}$, which also contributes to their capturing radicals.

4. Conclusions

This work suggests a physical–chemical model of detonation diamond formation, by which nanodiamonds are formed chemically, not via the phase transformation graphite → diamond. UFD are formed in the rarefaction region in a reaction mixture similar to those used for obtaining diamond films. A diamond nanoparticle has a complicated chemical composition. Properties of the medium detonation UFD are formed in and are typical of a liquid state of matter. A nanoparticle grows by the diffusion mechanism due to chemical reactions proceeding on its surface at adsorption of free hydrocarbon radicals. While a diamond particle is growing, its surface is permanently coated by hydrocarbon radicals and other compounds in the reaction volume. We have suggested a method of representing the reaction mixture state in the course of CC and UFD formation. It has been shown that CC amount in the products of detonation decreases with lengthening of the path run by the image point in the region below the line $H – CO$ and that the relative amount of UFD is defined by length of the path run in the diamond formation region. The model suggested gives a simple and adequate interpretation of available data on detonation synthesis of diamonds.

References