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Physical–chemical model of nanodiamond formation at explosion

A.P. Chernyshev^{a,c}, L.A. Lukyanchikov^b, N.Z. Lyakhov^a, E.R. Prueel^b, M.A. Sheromov^d,
K.A. Ten^b, V.M. Titov^b, B.P. Tolochko^{a,*}, I.L. Zhogin^a, P.I. Zubkov^b

^a*Institute of Solid State Chemistry and Mechanochemistry SB RAS, ul. Kutateladze 18, Novosibirsk 630128, Russia*

^b*Laurentiev Institute of Hydrodynamics, Novosibirsk 630090, Russia*

^c*Novosibirsk State Technical University, Novosibirsk 630092, Russia*

^d*Budker Institute of Nuclear Physics, Novosibirsk 630090, Russia*

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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 (DW) 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 (CC) 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 CC amount. Diamonds are formed by the free-radical mechanism in the unloading wave, beyond the Chapman–Jouguet plane, in a media close to a liquid state.

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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→diamond. Graphite turns into 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 a plasma. In doing so, 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, as ultra-fine diamonds (UFDs) were considered to arise directly in the detonation wave (DW), i.e. from free carbon at a temperature of 3000–3700 K and a pressure of 20–35 GPa. However, *in situ* investigation of dynamics of nanodiamond formation performed in work [1] demonstrated that UFD are formed in 500 ns after the SW front

passage, beyond the DW. Hence, the DW only creates the reaction mixture (plasma), from which diamonds are then formed in the course of chemical reactions. That is why detonation synthesis of UFD should be referred to the second group.

2. Formation of plasma in the DW

Conductivity of detonating high explosives (HE) has been presented in many works (e.g. see Ref. [1]). Dependence of conductivity, σ , on time, τ , can be described in terms of hot points (HPs) in the following way. After the shock wave (SW) front passage, conductivity is observed to grow monotonously for approximately 100–200 ns [1]. Thus, it would be reasonable to correlate the section ab in Fig. 1 with the initial stage of detonation: from formation of centers of explosive destruction—hot points (HPs) directly beyond the SW front (point a)—to involving most of the explosive into the chemical reaction (point b). At this stage, temperature and pressure keep growing

*Corresponding author. Tel: +8 383 339 41 45.

E-mail address: b.p.tolochko@inp.nsk.su (B.P. Tolochko).

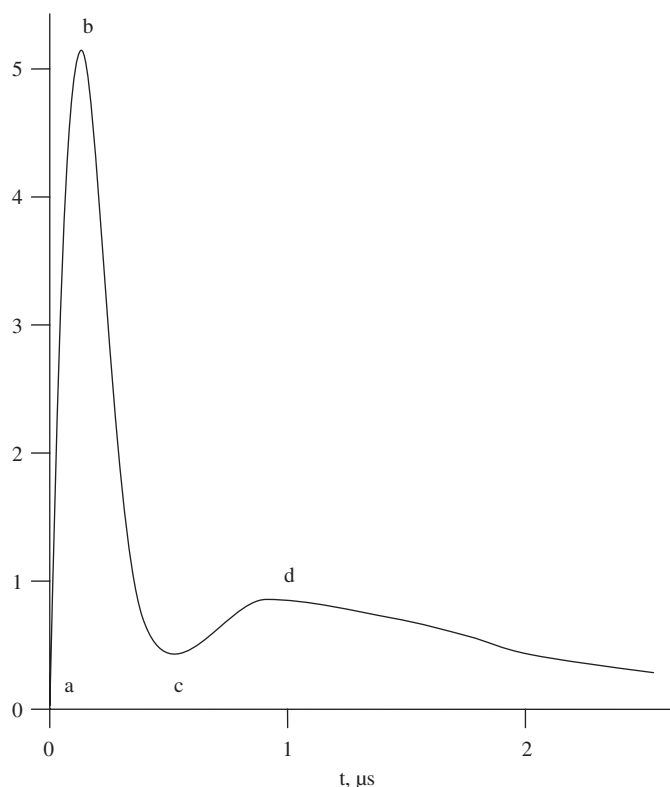


Fig. 1. The typical dependence of electric conductivity of TNT vs. time behind the shock front.

continuously, reaching their maximal values near point b. The time of spread of detonation products exceeds significantly the typical time of reaction. By 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.

3. Triangle diagram C–H–O and detonation synthesis of UFD

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 [2]. It was found empirically that diamond films only grow at compounds corresponding to a relatively narrow band along the line H–CO (Fig. 2). As we have shown in Ref. [1], UFD synthesis as such is preceded by a DW. That is why in this physical–chemical model, we suppose that at detonation diamond synthesis, activation is performed by a DW in a short time (300–500 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 the bc section (Fig. 1), no more new products of destruction come into the reaction space and comminution of reactant molecules is completed.

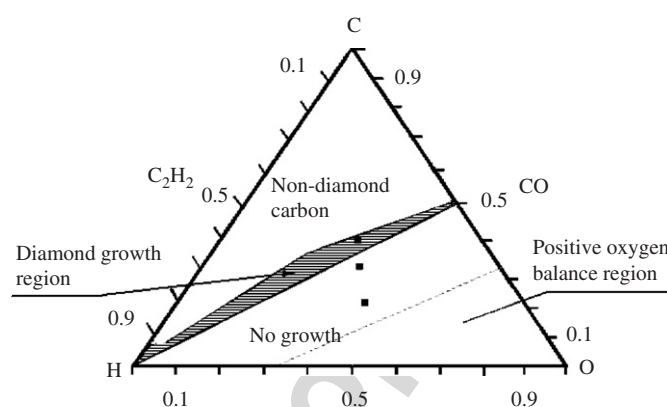


Fig. 2. The triangular diagram.

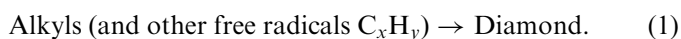
As oxygen partially leaves the reaction mixture in the form of explosion products (H_2O , CO_2 , CO , etc.), the ratio $[\text{C}]/([\text{C}] + [\text{O}])$ grows. In the triangle diagram C–H–O, this process results in continuous motion of the image point into the area with increasing relative amount of carbon in the reaction zone. For explosives of the $\text{C}_d\text{H}_b\text{N}_c\text{O}_d$ type, quantitative composition of the plasma is defined by chemical composition of the explosive. However, qualitative composition of the plasma changes only if the coefficient b or d equals zero.

For most HEs used for detonation synthesis of diamonds [3–5], the concentration ratio $[\text{C}]/([\text{C}] + [\text{O}])$ 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): $[\text{C}]/([\text{C}] + [\text{O}]) \approx 0.54$ and $[\text{H}]/([\text{H}] + [\text{C}]) \approx 0.42$. A corresponding point in the triple diagram lies in the diamond zone near the boundaries with the region where condensed carbon (CC) arises in its non-diamond forms. 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 CC ($m_1 = 15.7\%$) is almost 5 times less than after explosion of the following composition: trotyl—60%, hexogen—40% ($m_1 = 72.7\%$) (hereinafter data on UFD and CC content have been taken from Ref. [5]). For such explosive composition, we have $[\text{C}]/([\text{C}] + [\text{O}]) \approx 0.47$ and $[\text{H}]/([\text{H}] + [\text{C}]) \approx 0.5$. This point is below the diamond formation zone, which 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 reaction mixture composition passes through the diamond zone in its widest part. The relative amount of the diamond phase is defined by the width of the interval the image point passes over in the diamond formation zone.

4. Kinetics and thermodynamics of UFD formation

The main principle of chemical synthesis of nanodiamonds is the necessity of creating a chemical process

maintaining sp^3 hybridization. For a stationary plasma, i.e. a plasma of steady composition in a flow reactor, much depends on the atomic hydrogen. Though all bonds in the diamond volume have sp^3 hybridization, surface atoms of carbon have dangling bonds, that can associate themselves, turning into a state with sp^2 hybridization, which results in formation of non-diamond compounds (graphite, for instance). So, it is necessary to provide for a mechanism to prevent the rise of compounds with sp^2 hybridization. In the reaction mixture with hydrocarbon compounds, this function is performed by atomic hydrogen [6,7], which fills the dangling bonds. Hydrogen joins carbon with sp^2 hybridization faster than carbon with sp^3 hybridization, which stops graphitization of the surface. 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. Increasing reaction mixture pressure accelerates film growth due to higher concentration of free alkyl radicals and because of the shift of metastable thermodynamical equilibrium toward diamond phase by the Le Chatelier principle. In fact, chemical synthesis of diamonds is performed by the following scheme



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 DW method, besides functional oxygen-containing groups, a large amount of saturate hydrocarbon radicals were found [2,8,9]. 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. Thus a detonation diamond is formed in the course of chemical reactions (1) proceeding beyond the Chapman–Jouguet plane. The diamond growth rate can be estimated as the ratio of the average nanodiamond diameter (d) to the time of escape of nanodiamonds from the reaction volume (t_r). By data of work [1], the average diameter of diamond particles is 5 nm and t_r equals 0.5 μ s, whence we obtain $G = 0.01$ m/s. Using the Einstein formula, we immediately have the following estimate:

$$D \sim \frac{d^2}{t_r} \sim 10^{-10} \text{ M}^2/\text{c}. \quad (2)$$

So, properties of the medium where detonation UFD are formed are typical of a liquid state.

5. Conclusions

UFDs are formed beyond the Chapman–Jouguet plane in a reaction mixture similar to mixtures used for obtaining diamond films. A diamond cluster has a complicated chemical composition. A cluster 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, hydrocarbon radicals and other compounds in the reaction volume always coat its surface. A method of representing the reaction mixture state in the course of CC and UFD formation has been suggested. 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 the length of the path run in the diamond formation region. Properties of the medium detonation UFD are formed in are typical of a liquid state of matter.

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