

## 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.

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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, *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

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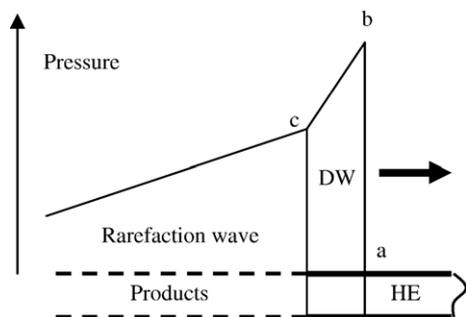


Fig. 1. The schematic of detonation wave.

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

Table 1  
Condensed products of explosion (from ref. [3])

Explosives	UFD/HE %	CC/HE %	UFD/CC %	$\frac{[C]}{[C]+[O]}$	$\frac{[H]}{[H]+[C]}$
TNT	2.8	18.1	15.7	0.54	0.42
TNT/hexogen 90:10	4.1	14.7	28	0.52	0.44
TNT/hexogen 70:30	8.3	12.4	66.9	0.49	0.48
TNT/hexogen 60:40	6.8	9.4	72.7	0.47	0.5
TNT/hexogen 50:50	7.2	9.2	78.4	0.45	0.52
TNT/hexogen 30:70	5.5	7.0	78	0.41	0.58
Hexogen				0.33	0.67

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

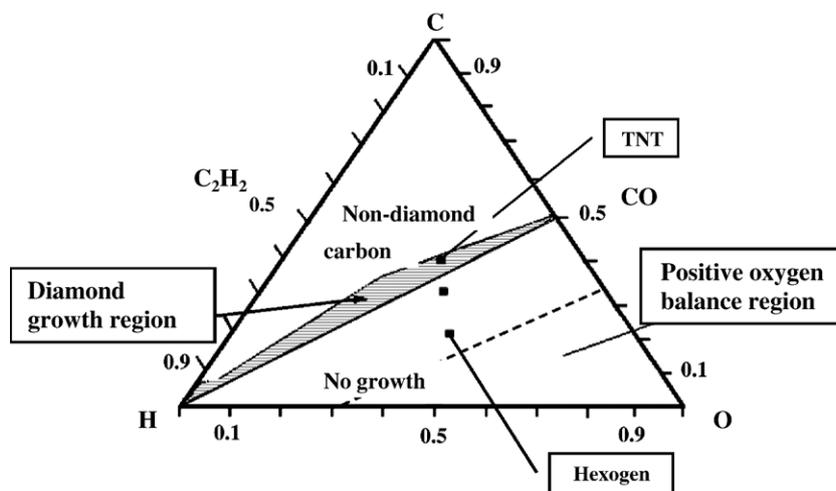


Fig. 2. The triangular diagram.

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