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Effect of Detonation Synthesis Conditions on the Phase Composition of Diamond

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Abstract—The phase composition of carbon produced by detonation synthesis was studied as a function of detonation conditions. The results demonstrate that, at an insufficient detonation power, the formation of diamonds may depend on the nature of the electron hybridization in the carbon atoms of the explosive. If the cooling rate of the detonation products is not high enough, the diamond yield may be notably reduced by amorphization.

INTRODUCTION

Shock and detonation waves are widely used to synthesize new materials. Negative-oxygen-balance detonation of carbon-containing explosives yields highly dispersed carbon in an amount governed by the equilibrium in the disproportionation of CO into C and CO_2. Under certain detonation conditions, the reaction products contain ultrafine diamond (UFD). The known procedures for extracting UFD from detonation products rely on the selective oxidation of more reactive, nondiamond carbon. Detonation-produced UFD finds wide practical application in the fabrication of polishing pastes, composite electroplates, and diamond-containing composites and films. Although considerable theoretical and experimental effort has been concentrated on detonation synthesis, additional work is still necessary to understand the detailed mechanisms of detonation and raise the efficiency of the process.

The products of trinitrotoluene ($C_7H_5N_3O_6$) + hexogen ($C_3H_6N_6O_6$) detonation are the best studied, since trinitrotoluene (TNT) is a carbon-rich explosive, and hexogen decomposition ensures a high pressure in the reaction system [1]. The composition of such explosives has a significant effect on the yield of condensed carbon, diamond content, and particle size of UFD. The results obtained in different studies are typically in good agreement, whereas their interpretations may differ drastically. For example, it was found by the radiotracer technique that diamond is formed mainly from carbon atoms of TNT, whereas the carbon of hexogen passes, for the most part, into nondiamond carbon [1–3]. Titov *et al.* [1] assumed that TNT decomposition is accompanied by the formation of diamond nuclei from bonded carbon groups just behind the front of the shock wave, that is, in the earliest stage of detonation. Kozyrev *et al.* [2] considered two possible reasons for the predominant formation of diamond from the carbon of TNT. One of them is that diamond particles are formed from TNT and hexogen at different rates. The other reason, supposed to be more likely, is the larger oxygen balance of hexogen and insufficient mixing of the detonation products. The higher conversion of hexogen to UFD at higher hexogen contents of the starting mixture was attributed to the enlargement of the diffusion-mixing zone [2]. According to Anisichkin [3], the low conversion of hexogen to diamond is associated with the higher hydrogen content in comparison with TNT. In the initial stage of transformations in the shock wave, diamond and methane are formed. Next, methane oxidizes yielding nondiamond carbon. Accordingly, the carbon of TNT passes mainly into diamond, and that of hexogen passes into nondiamond carbon.

It was found that, as the fraction of hexogen in the starting mixture increases, the UFD content of the detonation products first rises rapidly and then (at 40–50 wt % hexogen) remains virtually constant [4, 5]. Kozyrev and Golubeva [4] explained this finding by the fact that, at an insufficient power of the detonation wave, either only partial destruction of TNT molecules occurs and the resulting fragments are unfavorable for diamond formation or the rates of particle formation and growth are too slow, and a significant fraction of the carbon passes into nondiamond phases. After the threshold power of the detonation wave is attained, molecules break down into carbon-containing fragments that convert to diamond at a high rate. A further increase in hexogen content does not change the picture.

The effect of the retention medium is also interpreted in different ways. According to Savvakin and Trefilov [6], liquid media enable full retention of detonation products, whereas gaseous media lead to graphitization of the finest diamond particles, accompanied by a reduction in diamond yield and specific surface. Petrov *et al.* [7] found that, as the heat capacity of the detonation medium decreases, the specific surface of the resultant diamond powder increases, and the particle size decreases. According to Aleksenskii *et al.* [8], after the removal of nondiamond carbon under identical conditions, UFD obtained in a gaseous atmosphere contains a larger amount of an amorphous *sp*^{2} phase on diamond cores. The amorphous phase originates from the reverse transformation diamond $\longrightarrow$ graphite during cooling of the detonation products. High-resolution electron-microscopic studies demonstrate that the retention conditions and the initial density of the explosive charge have a significant effect on the structure of condensed carbon, consisting of extended and small graphite-like particles, amorphous carbon, and diamond particles [9].

It was also reported that the detonation product is nonuniform in its reactivity with nitric acid: the amorphous component oxidizes first; next, oxidation of graphite microparticles occurs. UFD particles are very nonreactive with nitric acid and oxidize with a very slow rate [10]. The separation of nondiamond carbon phases is impeded by the small particle size of these phases and the large exothermic effect of oxidation. By introducing special additions (boric anhydride) and adjusting the temperature of holding in air, we were able to develop a procedure for chemical phase analysis which makes it possible to quantitatively determine amorphous carbon, graphitic carbon, and diamond [11].

The purpose of this work was to study the effect of synthesis conditions on the structure of the detonation product and properties of UFD.

EXPERIMENTAL

We studied carbon powders produced by detonation of TNT + hexogen charges of the same weight and density in a 2-m^3 chamber and the UFD isolated from the synthesis products.

The relative contents of different carbon species were determined by chemical phase analysis [11]. X-ray diffraction (XRD) analysis was carried out with a DRON-3 diffractometer (CuK_α radiation, Ni filter).

UFD was isolated by oxidation of nondiamond carbon with atmospheric oxygen at 720 K in the presence of boric anhydride, followed by boiling in dilute (1 : 5) HCl. The treatment duration was adjusted based on the residual nondiamond-carbon content, which was no greater than 0.5%. The extraction product was washed with water to constant pH; the precipitate was separated and dried to constant weight at 380 K.

The specific surface was determined by nitrogen BET measurement. The equilibrium water content was determined gravimetrically at 290 K and 70% relative humidity. The surface properties of diamond particles in hydrosols were studied by selective neutralization, pH measurements, and macroelectrophoresis (the experimental conditions and calculation procedure were reported in [12]).

All of the reagents used were of pure grade. The data presented for the detonation product and UFD are averages over 4–6 samples. The confidence interval was calculated for a 95% confidence level using the Student distribution.

RESULTS AND DISCUSSION

The contents of nondiamond phases in the detonation product were found to depend on the TNT : hexogen ratio (Table 1). The mass yield of condensed carbon increases with TNT content, in agreement with earlier data [1, 4, 5]. The UFD content varies very little up to 60% TNT and decreases at higher TNT contents, similar to what was reported in [4, 5].

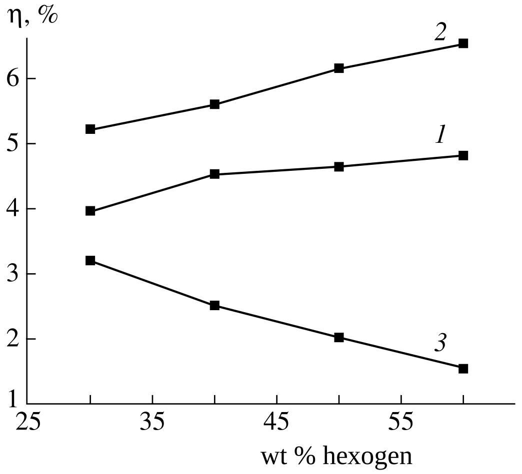
According to Kozyrev and Golubeva [4], the increase in the yield of condensed carbon with increasing TNT content is due to the smaller amount of oxygen in TNT compared to hexogen. The data in Table 1 can be used to calculate the yield of each carbon species as a function of the carbon content in the explosive charge. The results are shown in the figure.

It follows from these data that, under the conditions of this study, increasing the hexogen (and, hence, oxygen) content of the charge does not reduce the net yield of condensed carbon. Probably, the higher degree of oxidation is compensated by a shift of the reaction toward liberation of free carbon with increasing pressure.

The diamond yield varies nonmonotonically with hexogen content: at 40% hexogen, there is a plateau (curve *1*). The yield of the amorphous phase increases steadily (curve *2*). The yield of graphite-like carbon decreases with increasing hexogen content (curve *3*). These findings correlate with XRD data: with increasing hexogen content, the intensity of the 002 peak from graphite (2θ = 26°) decreases, and its asymmetry on the low-angle side becomes stronger, testifying to an increase in the content of disordered carbon. Since the

Table 1. Weight yield and phase composition of condensed carbon as functions of charge composition

wt % TNT	Carbon yield, %	Weight percent		
		UFD	amorphous carbon	graphite-like carbon
40	3.2	37	50	12
50	3.4	36	48	16
60	3.6	36	44	20
70	3.8	32	42	26



Yield of (*1*) UFD, (*2*) amorphous carbon, and (*3*) graphite-like carbon in terms of carbon vs. hexogen content of the explosive charge.

retention conditions (and, hence, the degree of graphitization) were kept unchanged, it is reasonable to expect that the yield of graphite-like, sp^2-hybridized carbon is influenced by the nature of the molecules of the explosive. Indeed, the formation of simple substances from atoms can be generally thought of as a two-step process: atom ⟶ cluster ⟶ crystal. The crystal structure is controlled by external influences—pressure and temperature. At the same time, the formation of diamond and graphite is, in large measure, influenced by hybridization (energetics of carbon atoms). For example, in the kinetic stability region, diamond is extremely difficult to deposit on a substrate if use is made of uni-, di-, and trivalent carbon atoms [13].

Depending on carbon hybridization in the starting carbon-containing compounds, two types of graphitization are distinguished: homogeneous (fast, without phase transformations) and heterogeneous [14]. Under dynamic compression to pressures above 20 GPa, the crystal lattice of graphite begins to break down, which is accompanied by changes in bonding configuration and nucleation of carbynes [15]. It would be expected that, below a certain power of the detonation wave, the forming carbon clusters retain the original type of hybridization. Therefore, the formation of diamond in the detonation zone may involve three steps: (1) carbon clustering, (2) changes in bonding configuration, and (3) formation of diamond particles. Which step will limit the rate of diamond formation depends on pressure, temperature, and the nature of the molecules of the explosive. During decomposition of hexogen (sp^3 hybridization of separated carbon atoms), the rate of the first step is slow, and diamond particles have no time to be formed. Increasing the power of the detonation wave increases the residence time of particles in the high-pressure zone; in this regime, the conversion of hexogen to diamond increases with hexogen content [2], but the first step still limits the rate of diamond formation from hexogen. During TNT decomposition in a detonation wave with a relatively low power, clusters are formed from already existing carbon groups, but the sp^2-hybridized state is partially retained, which inhibits diamond formation. Raising the pressure accelerates restructuring, and the diamond yield increases with hexogen content. A further increase in pressure may lead to more active dissociation of TNT molecules into constituent atoms, and the process will again be limited by the first step—clustering. In such a case, the break in the plot of the diamond yield vs. hexogen content (figure, curve *1*) may be associated with a change from one rate-limiting process to another.

The observed reduction in the yield of sp^2-hybridized (more highly ordered) carbon with increasing hexogen content (curve *3*) is attributable not only to the corresponding decrease in TNT content; calculations indicate that the ratio of this form of carbon to the carbon of TNT decreases with increasing hexogen content. It is therefore reasonable to assume that, with increasing pressure, the breakup of the hybridization configuration in TNT becomes predominant. The increase in the yield of the most disordered, amorphous carbon (curve *2*) can be explained in an analogous way: first, the contribution from the carbon of hexogen increases and, second, the graphite-like carbon becomes more disordered. Thus, the phase composition of the detonation product is governed by the nature of the explosive and the detonation parameters.

The formation of a large amount of disordered carbon at a low hexogen content may be associated with the poor retention of diamond in a CO_2 atmosphere. If the cooling rate is not high enough, the diamond formed is exposed to high temperature for a short time. Considering that the thermally induced conversion of diamond to graphite involves the formation of a disordered structure [16] and that the detonation time is very small, it is reasonable to assume that the dominant process is the breakdown of the diamond structure, without subsequent graphitization. Therefore, more effective cooling of the detonation products should reduce the content of amorphous carbon and raise the diamond yield.

The data in Table 2 illustrates the effect of the retention medium on the yield and composition of the detonation product obtained from a 60 : 40 mixture of TNT and hexogen. Improving the retention conditions increases the intensity of the 111 XRD peak from diamond ($2\theta \simeq 44°$) and reduces the intensity of the amorphous halo. The observed changes in phase composition lend support to the assumption that UFD is amorphized in CO_2. Moreover, the notably reduced yield of condensed carbon in CO_2 testifies to partial oxidation. Taking into account the data in Table 2 and the difference in oxidability between amorphous carbon (highly reactive) and UFD (inert), we conclude that the reduction in diamond yield is mainly due to amorphization.

Table 2. Weight yield and phase composition of condensed carbon as functions of the retention medium

Retention medium	Carbon yield, %	Weight percent		
		UFD	amorphous carbon	graphite-like carbon
CO_2	3.6	36	44	20
$CO_2 + H_2O$	6.0	44	33	23
H_2O	7.5	56	18	26

Table 3. Effect of the retention medium on the properties of UFD

Medium	S, m^2/g	N, mg-equiv/g	pH	$-\zeta$, mV	$[H_2O]$, %
H_2O	270	0.60 ± 0.03	5.8 ± 0.3	43.0 ± 0.6	2.5 ± 0.3
$CO_2 + H_2O$	280	0.70 ± 0.04	5.2 ± 0.2	41.0 ± 0.5	2.9 ± 0.2
CO_2	300	0.90 ± 0.05	4.6 ± 0.3	36.0 ± 0.5	4.0 ± 0.3

The retention conditions also influence the properties of the UFD isolated from the detonation products (the necessary heat treatment time was shorter at lower contents of graphite-like carbon, which is difficult to oxidize). Upon deterioration of the retention conditions, the specific surface S and equilibrium water content $[H_2O]$ increase slightly. This is accompanied by changes in the surface properties of the UFD particles—number of protogenic groups, N; electrokinetic potential, ζ; and pH of the hydrosol (Table 3). Clearly, partial oxidation in CO_2 increases the amount of oxygen-containing protogenic groups, thereby reducing the pH of the hydrosol. Increasing the number of functional groups capable of forming hydrogen bonds and acting as active centers for water adsorption increases the thickness of the hydrate shell on the surface of the hydrosol particles. The observed decrease in the magnitude of the electrokinetic potential of UFD particles in hydrosols is associated with the shift of the hydrodynamic slip boundary farther away from the particle surface into the aqueous medium. As the hydrophilicity of the surface increases, so does the hygroscopicity of the powder. Thus, the properties of UFD are influenced not only by the detonation conditions but also by the retention medium.

CONCLUSION

At an insufficient detonation power, the formation of diamonds may depend on the nature of the electron hybridization in the carbon atoms of the explosive. Increasing the hexogen content favors restructuring of the aromatic bonds in TNT. As a result, the diamond yield is determined mainly by the growth rate of diamond particles.

Deterioration of the retention conditions leads to diamond amorphization and partial oxidation of all the carbon species present. As a result, the diamond surface becomes more hydrophilic.

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