Transmission electron microscopy and x-ray diffraction studies of the detonation soot of high explosives

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Abstract. This paper presents the results of electron microscopy and x-ray diffraction studies of the recovered carbonaceous residue (soot) from the detonation of some high explosives: TNT, a mixture of TNT and RDX (50/50), benzotrifuroxane, and triaminotrinitrobenzene. The use of the same experimental setup allowed a qualitative and quantitative comparison of the detonation products formed under similar conditions. The results clearly show differences in the morphology of graphite-like and diamond inclusions and in the quantitative content of nanodiamonds for the explosives used in this study.

1. Introduction

The detonation products of various explosives with a negative oxygen balance contain a wide morphological and phase diversity of carbon forms. It is also known that the forms of condensed carbon in detonation products depend on the explosion conditions. The development of detonation methods for the synthesis of various forms of nanodiamonds is primarily motivated by their commercial and advanced applications. Wide use has been made of diamond-containing products consisting of quasi-spherical particles about 5 nm in diameter produced by detonation of a mixture of TNT and RDX (50/50), benzotrifuroxane, and triaminotrinitrobenzene. The use of the same experimental setup allowed a qualitative and quantitative comparison of the detonation products formed under similar conditions. The results clearly show differences in the morphology of graphite-like and diamond inclusions and in the quantitative content of nanodiamonds for the explosives used in this study.

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Therefore, in developing models for the detonation transformation of explosives, it is necessary to account for the condensed phase characteristic of the selected explosive and the explosion conditions. At the same time, there is a lack of data from direct measurements of the nucleation and dynamics of carbon particles behind the detonation front. This necessitates the addition of various hypotheses to numerical models.

The development of research methods using synchrotron radiation has made it possible to examine the dynamics of formation of nanodiamonds and their growth behind the detonation front [1–3], but the introduction of a number of assumptions is also required. In solving the inverse problem of reproducing the formation of nanodiamonds from small-angle x-ray scattering data, one assumes a spherical particle shape and typically a monodisperse size distribution. Investigation of the condensed residue, though not providing information on the state of carbon during the passage of the detonation front, provides detailed information on the final forms of carbon. In this work, the experimental setup was as nearly the same as possible to compare data on the recovered detonation products of various explosives. The charges used were identical to those investigated in [1, 4] using synchrotron radiation.

2. Experimental conditions
Detonators based on bulk PETN in an icy body were made to reduce the content of impurities. Initiation was performed by an auxiliary charge of PETN and HMX as they give an insignificant amount of condensed residue. The entire experimental assembly was frozen in ice with a total mass of about 1 kg. Detonation was carried out in an air-filled 50-liter explosion chamber of stainless steel.

For the experiments, cylindrical charges of 20 mm diameter weighing about 20 g were prepared. Cast charges of TNT and a 50/50 TNT/RDX mixture, commonly used for commercial production of nanodiamonds, and pressed charges of TATB and BTF were investigated.

Condensed detonation products mixed with water and crushed ice were collected and dried. The resulting samples were further purified (if necessary) by washing with acid to remove impurity metals or by annealing in air flow to remove amorphous carbon and graphite.

3. TEM studies
Transmission electron microscopy (TEM) micrographs were obtained with use of a JEM-2010 instrument (lattice resolution 1.4 Å, acceleration voltage 200 kV). Analysis of the local elemental composition was carried out using an energy dispersive x-ray (EDX) spectrometer equipped with a Si(Li) detector (energy resolution 130 eV). TEM data allow one to qualitatively establish the specific forms of carbon in the detonation products of the explosives studied and determine the typical linear size of inclusions, but it is worth noting that the resulting size will not be the mean one because of the complex form of carbon structures and because of the subjective preferences of the researcher. For the 50/50 TNT/RDX mixture, widely used in commercial production of nanodiamonds, the results are presented in figure 1. The condensed products contain a large amount of separate quasi-spherical nanodiamonds (the measured interplanar spacings corresponding to the diamond form of carbon are shown in the figure) with a typical size of about 5 nm, carbon fibers up to several tens of nanometers and onion-like carbon particles a few nanometers in diameter. The results are in good agreement with literature data, e.g., [5–7].

TEM images show (figure 2) that the detonation products of TNT contain carbon fibers (up to tens of nanometers) and non-spherical nanodiamond particles which are larger than those for the TNT/RDX mixture and have a size of about 10 nm or more. The amount of the diamond phase in the unpurified detonation products is substantially less than expected [8]. It should be noted that the larger diamond particles characteristic of TNT are also rare in the detonation products of the 50/50 TNT/RDX mixture. This is obviously due to the inhomogeneity of the mixture, which was also mentioned in [7, 9].
The samples obtained by detonation of TATB charges (figure 3) are characterized by the presence of mainly carbon fibers up to tens of nanometers and rare amorphous carbon structures with linear sizes up to several tens of nanometers. TEM images do not reveal the presence of nanodiamond particles. Similar results on the absence of nanodiamonds in the detonation products of identical charges were obtained in a study [4] of the dynamics of carbon condensation behind the detonation front using small-angle x-ray scattering of synchrotron radiation. The integrated intensity of small-angle x-ray scattering on detonating TATB charges was lower than that in TNT detonation and significantly lower (by more than 2-fold) than for 50/50TNT/RDX charges. In the cited paper, the average diameter of the scattering centers behind the detonation front for TATB charges is reported to be 2.6 nm (for comparison, for TNT/RDX charges, 4.6 nm in the same work), and it is concluded that these regions of density fluctuations have a non-diamond carbon structure. The presence of nanodiamonds is assumed, but their amount and characteristic sizes are lower (less than 2 nm) than the resolution of the experimental setup.
Figure 3. TEM micrographs of TATB: a—carbon fibers (tens of nanometers in length); b—amorphous carbon particles (tens of nanometers in diameter).

Figure 4. TEM micrographs of BTF: large spherical particles (hundreds of nanometers).

The absence of nanodiamonds in the TATB detonation products is not consistent with the literature data we are aware of. Thus, in [10], the measured percentage yield of nanodiamonds for pressed charges of TATB was 2.08% of the initial weight of the explosive. High content of nanodiamonds was also detected in TATB/HMX mixtures [11]. However, the conditions of the experiments in these studies were different. In [10], the diameter of TATB charges (40 mm) was two times greater, and in [11], the weight of the initial charge (310 g) was more than ten times higher. At the same time, synchrotron radiation studies of carbon condensation in TATB/HMX charges of 20 mm diameter showed no significant difference in carbon condensation for different proportions of the components [1].

The condensed products of detonation of benzotrifuroxane are mainly large round particles up to a few hundred nanometers in diameter (figure 4a). According to TEM analysis, these particles have a heterogeneous internal structure (figure 4b). Detection of nanodiamonds in the unpurified products is difficult, since the diamond core cannot be seen due to the thick layer of non-diamond carbon on the surface.

In the literature, there are data on the detection of nanodiamonds in the detonation products of BTF using various methods. Thus, in a study [12] of detonation of BTF charges weighing...
Figure 5. TEM micrograph of semi-purified BTF soot. Some large spherical particles have a complex structure.

Figure 6. TEM micrographs of purified BTF soot: a—complex-shaped nanodiamonds; b—single-crystal nanodiamond (up to 100 nanometers).

1000 g, x-ray structural analysis indicates the presence of the diamond phase, and in [13], the presence of nanodiamonds in the detonation products of BTF charges weighing 100 g is confirmed by TEM. The presence of significant amounts of the diamond phase of carbon behind the detonation front was also confirmed by a synchrotron radiation study [1] of detonating BTF charges of 20 mm diameter. To confirm the presence of nanodiamonds by TEM, the initial samples were purified from other carbon phases by annealing in air flow.

An intermediate result of annealing at a temperature of 460 °C is presented in figure 5. In the TEM micrograph, one can see that the large particles have a complex internal structure and, after removal of part of the amorphous and graphite phases of carbon, their shape remains spherical.

Further increase in the annealing temperature to 515 °C results in a nearly complete disappearance of the non-diamond phase. TEM observations show complex-shaped diamond particles, some of which have a single-crystal structure with linear sizes up to 100 nm (figure 6b). In the center of the image (figure 6a) there is a polycrystalline diamond particle with a diameter of more than 100 nm which retains its spherical shape. This confirms the conclusion of [12] that
Figure 7. TEM micrographs of BTF soot. Large spherical particles with an onion-like structure: a—with a homogeneous internal structure; b—with a large number of inhomogeneities.

In BTF detonation, nanodiamonds are formed from a liquid carbon phase; the porous structure of the products suggests the presence of several points of growth of the diamond phase.

In the unpurified carbon residue of BTF, there are carbon particles of regular spherical shape consisting of carbon layers covering each other (figure 7a). The layered shape of the particles is similar to the onion-like structures observed for the TNT/RDX mixture, but the size of the particles is much larger—up to 100 nm. Some particles contain many inhomogeneities and the carbon layers are broken and entangled (figure 7b).

4. X-ray diffraction data

X-ray diffraction (XRD) patterns were obtained with HZG-4S (Germany) using Co K$_\alpha$ radiation in a 2Θ scanning range of 20–100°.

The recovered detonation products contain a large number of components. Metal impurities resulting from shock wave impact on the walls of the explosion chamber and from other causes are present in addition to various forms of carbon. As a result, the XRD pattern of the initial detonation products has many peaks (including overlapping ones) corresponding to various substances and their modifications, which hinders accurate interpretation of the results.

Metal impurities were removed from the detonation products by washing with acid—a standard method which allows the recovery of primarily diamond particles due to their low reactivity. Acid treatment of the detonation products at elevated pressure and temperature also reduces the content of the non-diamond carbon phase; in this case, this was not required.

The resulting XRD patterns are presented in figures 8 and 9, where the arrows indicate the angles 2Θ for the diamond modification of carbon. The relative height of the peaks allows a qualitative determination of the percentage of the diamond phase in the samples. Thus, in the samples obtained by detonation of 50/50 TNT/RDX, the yield of the diamond phase is substantially higher than that for pure TNT, whose unpurified detonation products also contain nanodiamonds, as confirmed by TEM observations. For TATB, this peak is almost indistinguishable from noise, indicating the possible presence of only trace amounts of nanodiamonds or their small (less than 2 nm) size, which is not sufficient to collect statistics on lattice scattering. According to XRD data, the detonation products of BTF contain a significant amount of the diamond phase of carbon, although, according to TEM, it is almost absent from the unpurified products. Given the overall morphology of the condensed residue of BTF, diamond structures should be present in large amounts in large spherical particles.
Figure 8. XRD pattern of the purified detonation soot of 50/50 TNT/RDX (on the left-hand side) and TNT (on the right-hand side): peaks corresponding to nanodiamonds are marked by black arrows.

Figure 9. XRD pattern of the purified detonation soot of TATB (on the left-hand side) and BTF (on the right-hand side): peaks corresponding to nanodiamonds are marked by black arrows.

For all soot samples, except for TATB, there is a broadening of the diffraction peaks corresponding to the diamond phase of carbon. As a rule, this is due only to the small sizes of the regions of coherent scattering (RCS). RCS sizes were estimated by the Williamson–Hall method [14]. Given a quasi-spherical particle shape, it can be assumed that the RCS size corresponds to the average particle size. For TNT and the TNT/RDX mixture, this assumption seems quite reasonable. For BTF, such an assumption cannot be made.

The estimated linear sizes of the RCS and those observed from TEM data are shown in table 1. For TNT/RDX and TNT, commonly used for the synthesis of nanodiamonds, the obtained values are in good agreement with literature data. Although the observed typical size of diamond particles is significantly larger for pure TNT than for the TNT/RDX mixture, the RCS sizes for these samples are the same, which is explained by the non-spherical shape of nanodiamonds in the TNT detonation products. In the detonation of TATB charges of 20 mm diameter, nanodiamonds with sizes larger than 2 nm were not observed; the detection of diamond particles of smaller sizes is beyond the accuracy of the equipment, so that their
Table 1. Nanodiamonds in detonation products.

| Explosive   | XRD d, nm | TEM d, nm |
|-------------|-----------|-----------|
| TNT/RDX 50/50 | 3         | 5         |
| TNT         | 3         | 10        |
| TATB        | < 2?      | < 2?      |
| BTF         | 15        | up to 100 |

presence is possible. The porous form of nanodiamonds in the detonation products of BTF is responsible for the significant difference between the XRD data and TEM observations. In addition, it is worth noting that in [12], the average RCS size for the detonation products of a BTF charge weighing 1000 g is 31 nm, which is twice that obtained in our study for a charge weighing about 20 g.

5. Conclusions
The condensed detonation products (soot) of the investigated explosives contain a large amount of various forms of carbon. In addition, each of the soot samples has distinguishing features. The detonation soot of pure TNT is characterized by the presence of nanodiamonds of polyhedral shape with a size of about 10 nm and carbon fibers up to tens of nanometers which, based on the measured interplanar spacing, correspond to the graphite modification of carbon. The detonation products of the 50/50 TNT/RDX mixture contain smaller nanodiamonds of quasi-spherical shape with a diameter of a few nanometers, onion-like carbon of the same size, and carbon fibers up to several tens of nanometers long. The TATB detonation carbon consists mainly of carbon fibers up to tens of nanometers long and slightly separated particles of amorphous carbon with sizes up to tens of nanometers. The BTF charges are characterized by the presence of large spherical carbon particles up to several hundred nanometers in diameter. These particles were initially composed of a liquid carbon phase, but their condensation followed different pathways, resulting in both perfect and considerably inhomogeneous onion-like particles up to 100 nm in diameter and porous diamonds.

The variety of carbon forms in the detonation products of various explosives and their dissimilarity indicates significant variations in the detonation process. A comparison with published data shows that for the same explosive, the detonation products can be significantly different in different experimental setups. The original TEM data are available online [15].

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References
[1] Ten K A, Titov V M, Pruuel E R, Kashkarov A O, Tolochko B P, Aminov Yu A, Loboyko B G, Muzyrya A K and Smirnov E B 2015 Proc. 15th International Symposium on Detonation. Publication No. ONR-43-280-15 (San Francisco, California) pp 369–374
[2] Ramos K J, Jensen B J, Iverson A J, Yeager J D, Carlson C A, Montgomery D S, Thompson D G, Fezzaa K and Hooks D E 2014 J. Phys.: Conf. Ser. 500 142028
[3] Bagge-Hansen M, Laudersbach L, Hodgkin R, Bastea S, Fried L, Jones A, van Buuren T, Hansen D, Benteron J, May C, Graber T, Jensen B J, Harisky J and Wiley T M 2015 J. Appl. Phys. 117 245902
[4] Ten K A, Titov V M, Pruuel E R, Lukyanovich I A, Tolochko B P, Zhogin I L, Aminov Yu A, Filin V P, Loboyko B G, Muzyrya A K and Smirnov E B 2010 Proc. 14th International Symposium on Detonation. Publication No. ONR-351-10-185 (Coeur d’Alene, Idaho) pp 387–391
[5] Greiner N R, Phillips D S, Johnson J D and Volk F 1988 Nature 333 440–442
[6] Kuznetsov V L, Chuvilin A L, Butenko Yu V, Mal'kov I Yu and Titov V M 1994 Chem. Phys. Lett. 222 343–348
[7] Tao X, Kang X and Jiazheng Z 1996 Mater. Sci. Eng. B 38 L1–L4
[8] Titov V M, Anisichkin V F and Mal'kov I Yu 1989 Combust., Explos. Shock Waves 25 372–379
[9] Chen P, Huang F and Yun S 2003 Carbon 41 2093–2099
[10] Petrov E A, Baraboshkin K S, Bychin N V, Larionov B V and Bayramian I V 2012 Proc. Ultrafine Powders, Nanostructures and Substances: Production, Properties and Applications. VI Stavers’s Readings (Krasnoyarsk, Russia) pp 14–15
[11] Anisichkin V F, Mal’kov I Yu and Sagdiev F A 1991 Proc. V-th All-Union Meeting on Detonation vol 1 (Krasnoyarsk, Russia) pp 27–30
[12] Mal’kov I Yu, Filatov L I, Titov V M, Litvinov B V, Chuvilin A L and Teslenko T S 1993 Combust., Explos. Shock Waves 29 542–544
[13] Batsanov S S, Osavchuk A N, Naumov S P, Efimov A E, Mendis B G, Apperley D C and Batsanov A S 2015 Propellants, Explos., Pyrotech. 40 39–45
[14] Williamson G K and Hall W M 1953 Acta Metall. 1 22–31
[15] Kashkarov A O, Pruuel E R, Ten K A and Zubkov P I 2016 Transmission electron microscopy of detonation carbon. Photo album. Tnt/rdx, bjf, tnt, tab