

## Carbon condensation in detonation of high explosives

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**Abstract.** This paper presents experimental data on monitoring of condensed carbon nanoparticle sizes in detonation of oxygen-deficient high explosives (HEs). The nanoparticle sizes were derived from processing of measured distributions of small-angle X-ray scattering (SAXS). The work was carried out at the accelerator complex VEPP-3 (BINP). The measured sizes of carbon nanoparticles are  $\sim 2$  nm in TATB and up to 3-5 nm in BTF in the chemical reaction zone. Carbon nanoparticles of maximum size are found beyond the chemical reaction zone and are as large as  $\sim 3$  nm in TATB and its mixtures with octogone (HMX) and  $\sim 70$  nm in BTF. The measured nanoparticle sizes coincide with the dimensions of nanodiamonds extracted from saved products of detonation (soot) of explosive charges of similar size and composition, which were exploded in an ice shell.

### Introduction

The studies of carbon condensation in detonation of oxygen-deficient HEs were initiated at The Lavrentiev Institute of Hydrodynamics (LIH) in 1983 in the context of works on synthesis of detonation nanodiamonds. These works were actively carried on at many centers. Now there are over 800 papers on the subject in the world <sup>1, 2</sup>. The weight of explosive charges under study was 200 grams to several hundred kilograms; their diameter was 40 mm and more. It was mostly the saved detonation products (soot) collected after explosion in explosion chamber that was investigated in these works. Equipment of that time did not allowed investigation into the kinetics of carbon condensation, and therefore the time and place of condensation were

considered to coincide with the chemical reaction zone, because the medium parameters there corresponded to the stable phase of diamond.

The interest in this work increased due to the expansion of studies of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) at nuclear research centers in the USA and Russia in the mid 90s. The measured velocities of plates thrown using TATB were in better agreement with calculations if the energy release continued behind the detonation front. Calculations showed that the total time of carbon condensation by an order of magnitude exceeded the time of existence of the chemical reaction zone <sup>3, 4</sup>.

In the early 2000s, researchers in Novosibirsk began developing a new technique to study fast processes using high-energy accelerators. The high intensity of synchrotron radiation (SR) allowed

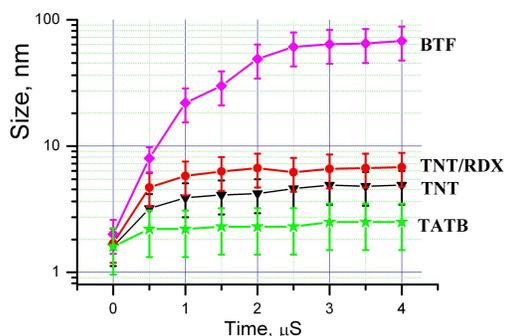


Fig. 1. Growth of the nanoparticle size in detonation of BTF, TNT, TNT/RDX and TATB against time. The particle sizes are shown on a logarithmic scale.

recording the dynamics of diffractive scattering distribution with an exposure of 1 ns<sup>5, 6, 7, 8, 9</sup>. The intensity of small-angle X-ray scattering (SAXS) is proportional to fluctuations of electron density, which is in connection with carbon condensation in detonation of oxygen-deficient high explosives. Simulation calculations showed that the measured distributions of small-angle X-ray scattering (SAXS) could be used for derivation of information about the size of carbon nanoparticles that condense in the chemical reaction zone and beyond it<sup>6, 7, 8, 9</sup>.

This paper presents experimental data from a study of dynamics of carbon condensation in new compounds based on TATB, as well as benzotrifuroxan ( $C_6N_6O_6$ , BTF), a hydrogen-free HE. A study of TNT and a TNT/RDX mixture was carried out for comparison. The explosive charges in these experiments were of identical geometric dimensions. The experimental assemblies were also of equal dimensions (for ensuring identity of the spread of detonation products). Besides, all the explosive charges were small (diameter: 20 mm; length: 30 mm; weight: ~ 20 grams), while the literature offers data only for large charges<sup>1, 2</sup>. For the sake of comparison, charges of the same HEs of the same size were exploded in an ice shell in explosion chamber and the explosion products were saved. The soot was analyzed using microscopic and diffraction techniques.

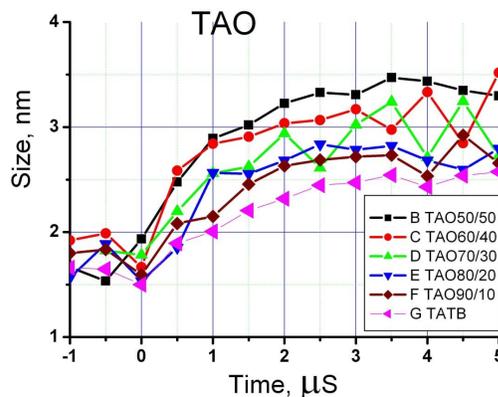


Fig. 2. Nanoparticle size dependence on time in detonation of TATB + HMX mixture.

#### SAXS measurement experiments and their results

The SAXS measurements were carried out on VEPP-3 beam line 0. The experimental set-up is described in<sup>7, 8, 9</sup>. SAXS (pulse duration: 1 ns) was recorded with detector DIMEX-3 with an angular resolution of  $10^{-4}$  rad<sup>10</sup>, located in 1 m from explosive charge.

The pressed samples of explosives made of TATB and its mixtures with HMX and ultradispersed diamond (UDD), as well as the samples of trinitrotoluene (TNT) and its mixtures with RDX, were of one size (diameter: 20 mm; length: 30 mm). As for hydrogen-free HEs, benzotrifuroxan (BTF) was investigated. The charges were pressed up to 95% of their maximum density.

The recorded SAXS distributions for mixtures of TATB and TNT were processed in the Guinier approximation<sup>11, 12</sup>. The intensity  $I(q, R)$  has the following form:

$$I(q, R) = I_0 \cdot \exp\left(-\frac{(qR)^2}{5}\right)$$

(scattering for spherical particles)

where  $q = \frac{4\pi \sin \Theta}{\lambda}$  is the wave vector, in which  $2\Theta$  is the scattering angle, and  $\lambda$  is the wavelength;  $R$  is the particle radius. Fig. 1 shows the resulting nanoparticle size dependence on time for TATB, TNT, TNT/RDX and BTF. At the initial moment (zero in the X axis corresponds to the detonation

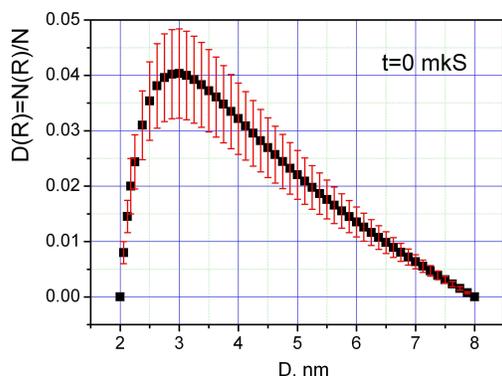


Fig. 3. Nanoparticle size distributions in the BTF detonation front. The error is highlighted red.

front), the nanoparticle size ranges from 1.5 nm in TATB to 3 nm in BTF. Derived from the scattering measured beyond the detonation front ( $3 \mu\text{s}$  later), the maximum particle size is  $\sim 2$  nm in TATB, 4 nm in TNT, 5 nm in TNT/RDX and 70 nm in BTF. In the TATB/HMX 50/50 mixture (fig. 2), the maximum particle size was  $\sim 3.5$  nm.

The recorded sizes of scattering nanoparticles in TATB and its mixtures with HMX were much less than those in TNT and its mixtures with RDX.

In detonation of BTF, the SAXS distribution measured can be processed with the software code GNOM<sup>13</sup>, because the SAXS signal amplitude in BTF is 4 times higher than that in TNT. The obtained nanoparticle size distributions are shown in fig. 3 and fig. 4. The figures present the relative numbers of particles of a certain size in relation to the total number of particles at any given time. In the detonation front, the size distribution peak falls on 3 nm, and in  $3 \mu\text{s}$  it moves to 30 nm.

### Saved explosion products

We also conducted experiments to analyze the saved detonation products of identical explosive charges. The charges were exploded in an ice shell in a hermetic stainless steel explosion chamber. The charge weight was  $\sim 20$  g; its diameter and length were 20 mm and 30 mm, correspondingly. The ice mass and diameter were 2000 g and 100 mm. The explosions were initiated using ten powder in a case

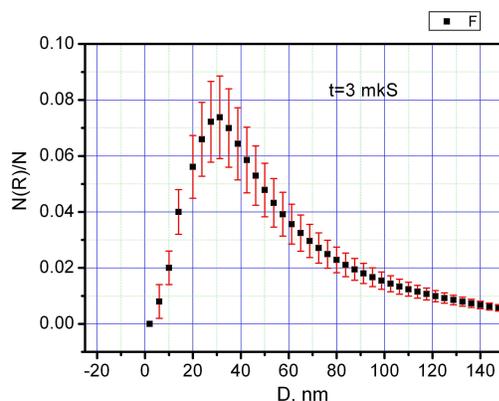


Fig. 4. Nanoparticle size distributions behind the BTF detonation front 3 microseconds after.

made of TNT/RDX 50/50 alloy. After explosion the chamber was washed with water and combustion products were merged into a vessel. After evaporation of water there was black slime left, so called soot (explosion products).

The resulting products were subjected to microscopic and diffraction examination. Nanodiamonds were isolated from the soot in a conventional way – acid treatment and blowing with hot gas (mixture of oxygen and high purity nitrogen) of a predetermined temperature. The gas at the exit was analyzed with XRF spectrograph for the presence of carbon combustion products. When  $CO$  and  $CO_2$  were no longer detected, the soot was analyzed using microscope and diffractometer, and then the gas temperature was increased by another  $50^\circ\text{C}$ . After heating up to  $520^\circ\text{C}$ , there were only nanodiamonds left in the soot. The maximum size of the nanodiamonds was  $\sim 5$  nm in the TNT products,  $\sim 4$  nm in the TNT/RDX 50/50 products and  $< 2$  nm (at the limit of resolution) in the TATB products.

A photo of BTF soot after heating up to  $420^\circ\text{C}$  is shown in Fig. 7. One can see four types of formations in the photo. Zone 1: amorphous carbon with inherent globe structure; the particle sizes are 100 to 1000 nm. Zone 2: impurity particles. They consist mainly of Fe-O. Zone 3: carbon modification (nanodiamond); small particles. The characteristic size is 2 to 10 nm. Zone 4: carbon modification (nanodiamond); large particles. These flattened-shape

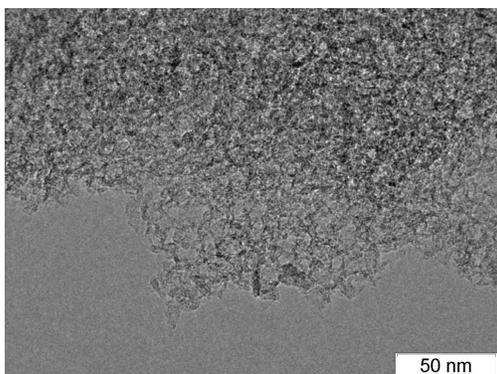


Fig. 5. Carbon nanoparticles in TATB detonation products.

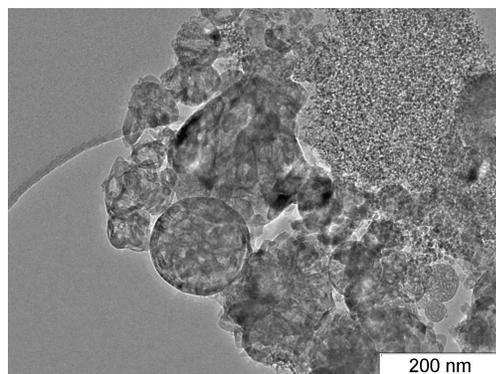


Fig. 6. Carbon nanoparticles in BTF detonation products.

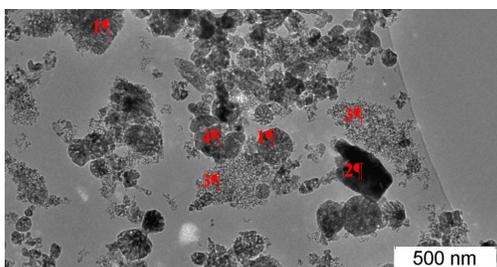


Fig. 7. BTF detonation products after heating up to 420° C

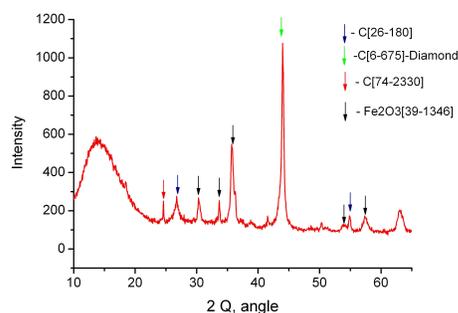


Fig. 8. Diffraction pattern of BTF detonation products after heating up to 420° C.

particles are 20 to 100 nm in size.

After heating up to 520° C, there were only nanodiamonds left in the BTF soot (Fig. 8). The obtained distributions of nanodiamond sizes in the studied HEs coincide with the distributions obtained in dynamic experiments (from SAXS measurements).

### Discussion

Our experiments have a characteristic feature of the small size of the explosive charges (diameter of 20 mm and weight of ~ 20 g). The nanodiamond sizes of ~ 4-5 nm in TNT and TNT/RDX 50/50 are nevertheless in agreement with the literature data.

From the SAXS data on TATB and in the saved TABT products, the nanoparticle size is ~ 2 nm, which is at the limit of resolutions of both the methods. Adding RDX in TNT leads to a marked increase in the yield of nanodiamonds<sup>1, 2</sup>; in case of TATB, adding HMX has little effect on the size of resulting nanodiamonds. Perhaps, in this size (about the limit diameter), the condensation is incomplete, although measurements of detonation parameters in the same TATB dimensions gave the same parameters as for large charges<sup>7</sup>. In<sup>14</sup>, there were nanodiamonds of ~ 3-4 nm found in the TATB detonation products of 40 mm in diameter. That is, this HE demonstrates a full-scale effect, which requires further study.

Large sizes of nanodiamonds in BTF were first noted in <sup>15</sup>. In the present paper, the size distribution of nanodiamonds was obtained for the first time. The large size of nanodiamonds is probably greatly influenced by the higher temperature in the detonation front, although the temperature measured in the BTF detonation front ( $\sim 4100^\circ\text{C}$  <sup>16</sup>) turned out to be less than expected. It is the duration of this temperature ( $\sim 1\ \mu\text{s}$ ) that is more important. It exceeds the chemical reaction zone by far. Since there is no hydrogen in BTF, the process of nanodiamond synthesis goes without intermediate radicals C-H, which usually slow down nanodiamond synthesis in conventional HEs.

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