The growth of carbon nanoparticles during the detonation of trinitrotoluene

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Abstract. In this work we present experimental data on measuring distributions of small-angle X-ray scattering (SAXS) during cast trinitrotoluene (TNT) detonation of 30 and 40 mm in diameter. Dynamics of average size of condensed carbon nanoparticle inkrises has been restored from experimental SAXS data. The work was carried out at the SYRAFEEMA (Synchrotron Radiation Facility for Exploring Energetic Materials) station at accelerator complex VEPP–4M (Budker Institute of Nuclear Physics). We observe minimal size of particles of order of 2 nm directly behind the detonation front. Later, the average size of carbon nanoparticles increases within 4–12 µs and reach values of 6 nm.

1. Introduction

In the early 2000s, studying of triaminotrinitrobenzene (TATB) in the nuclear centers of Russia and USA renewed interest of carbon condensation at detonation of high explosives (HEs) with negative oxygen balance. The results [1, 2] have shown that the assumption of the additional allocation of energy behind a chemical reaction zone better describes the experimental data on acceleration of the metal plates. The results of experiments can be explained by the additional energy released due to the exothermic coagulation of carbon clusters.

At the same time there were the first experiments on the dynamic registration of small-angle X-ray scattering (SAXS) distributions, which showed a long signal growth in the detonation of a mixture of trinitrotoluene (TNT) and hexogen (RDX) 50/50 [3].

The SAXS signal carry the information about the variations of density inside the investigated sample. This method is widely used for the static analysis of structure of dispersion sistems. In [3–5], it was shown that the integral SAXS signal increases with increasing negative oxygen balance. At raying of explosion products by synchrotron radiation (SR), the condensed carbon nanoparticles plays role the density variations.

The ability to use short high-periodical SR flashes of high-energy accelerators allowed us to reveal the time evolution of the signal at detonation of HEs. One can restore the dynamics of
the average particle size of the condensed carbon at detonation of HEs from the SAXS data [6].

Presently, registration of SAXS signal is the only way to register experimentally the dynamics of the size of the condensed carbon nanoparticles during detonation of HEs [7–9].

A new experimental station on accelerator complex the VEPP-4M put into operation in 2015. These new SYRAFEEMA station give much higher SR intensity than the similar station “Extreme States of Matter” on the VEPP-3 accelerator complex. It allowed us to X-ray examination of explosive charges of larger diameter (till 40 mm) and increase in the mass of the charges studies by ten times till 200 grams [6].

Similar experiments was carried out at Advanced Photon Source (Argonne National Laboratory, USA). In these studies, the hexanitrostilbene detonation produces carbon particles with radius of gyration of 2.7 nm, which corresponds to the 7 nm diameter of spherical particles. That particles was registered in 400 ns and remained constant in several next microseconds. It should be noted, that small charges of ≈ 6 mm in diameter were used in their study [9].

Dynamics of carbon condensation in big charge are still remains an actual problem. Here we present the experimental data on particle size dynamics during TNT detonation of charge of different diameter. The study of TNT is important because this explosive is the main component of mixtures used in the commercial production of ultrafine diamonds.

2. Experimental setup

The SAXS measurements were carried out at SYRAFEEMA station on the VEPP-4M. For dynamic experiments on registration SAXS, the scheme of measurement is shown in figure 3. The Kratky collimator was installed ahead the explosion chamber. It consist of lower K₁ and upper K₂ knives which formed initial SR beam. Straight beam was cut off by knife K₃ ahead the detector. The scattered rays detected by the detector DIMEX [10] with an angular resolution of 3⋅10⁻⁵ rad. Changing the position of all three knives was tuned by the micropositioner with accuracy 3 µm. After that, the SR beam size was 0.5 mm in thickness (figure 4 (1)) and 25 mm in width. The distance from knives K₂ and K₃ to the detector was 4660 and 231 mm, respectively. The time between frames was 600 ns.

The position of knife K₃ was chosen such that the angular measurement range to be 2–200 detector channels (0.06–5.8 mrad). This SAXS measurement range allowed to register particles of carbon of a diameter of D: dₘᵢₙ ≤ D ≤ dₘᵃₓ. dₘᵢₙ = π/qₘᵃₓ = λ/4 sin(θₘᵃₓ) ≈ 2 nm, dₘᵃₓ = π/qₘᵢₙ = λ/4 sin(θₘᵢₙ) ≈ 100 nm.

Figure 1 presents the spectral characteristics of the radiation of SYRAFEEMA station (real spectrum). The real spectrum of SR at the station depends on the wiggler emission spectrum, the absorption spectrum of the charge, and the detection efficiency of the DIMEX-3 detector. Calculations have shown the possibility of using such a polychromatic spectrum to restore the size of the scattering centers by replacing the real radiation spectrum to effective photon energy. The effective photon energy was determined by the least squares method so that the deviations between the SAXS signal with the real spectrum and the SAXS with the effective energy was minimal. Thus, we obtained an effective X-ray energy of 38 keV (see figure 2). At this energy, the SR wavelength is equal to λ = h c / E₀ = 0.0326 nm. The monochromatic radiation energy that most closely describes the SAXS from the real spectrum at the station is considered as the effective energy.

3. SAXS measurement experiments

The sizes of the scattering centers were determine using the Guinier approximation – I(q, R) = I₀ exp(−q²Rᵧ²/3), where Rᵧ is the radius of gyration of the particle, q = 4π sin(θ)/λ is the scattering vector, λ is the scattered radiation wavelength and 2θ is the scattering angle [11, 12]. For a spherical homogeneous particle of radius R, Rᵧ = √3/5 R.
Figure 1. Real radiation spectrum at the SYRAFEEMA station.

Figure 2. SAXS with consideration of the spectrum and effective energy.

Figure 3. Scheme of experiments on SAXS measuring.

Taking the logarithm of the intensity \( \ln(I(q, R)) = \ln(I_0) - q^2 R^2/5 \), we obtain a function which decreases linearly versus \( q^2 \). We can determine the size of the spherical particle \( D = 2R = 2\sqrt{-5k} \) using the slope \( k \) of this line [11,12].

Testing the possibility of using SR in dynamic explosive experiments was tested under static conditions on the scattering of the ultra-fine diamonds (UFD) (figure 4(2)). UFD particles were placed in the center of the explosion chamber instead of explosion charge. Transmission electron microscopy shows the average size of these particles is 5 nm. Analysis of SAXS distributions from UFD was determined using Guinier approximation. The slope was \( k \approx -1.4 \) (figure 5), this slope corresponds to the particle size of \( D = 5.4 \) nm. It can be seen that the graph of \( \ln(I) \) versus \( q^2 \) is different from a straight line. This means that the scattering centers have different sizes. The approximation by a straight line is applicable for the average particle size.

Test experiments have shown the ability to determine the particle size distribution obtained by treating the SAXS signal on the VEPP-4M. During TNT detonation scatter occurs on the particles of condensed carbon in the explosion products.

In our experiments we used cast samples of TNT of the same size (40 mm in diameter and 60 mm in length) and of density 1.6 g/cm³. The SAXS intensity distributions during the detonation of TNT are shown in figure 6. Each colored line represents the distribution of SAXS signal at a certain time. The sequence of the angular distributions gives the time dependence of dynamics.
Figure 4. Setting: 1 – attenuated straight beam, 2 – scattering on particles of ultra-fine diamonds (UFD).

Figure 5. The dependence of $\ln(I)$ on $q^2$: 1 – $\ln(I)$, 2 – approximation by straight line for UFD ($k \approx -1.4, D \approx 5.4$ nm).

Figure 6. SAXS data during TNT detonation in the first 2.5 $\mu$s for one experiment.

Figure 7. 1 – SAXS for TNT detonation at 6 $\mu$s behind the front, 2 – Guinier approximation.

Figure 8. Dynamics of the average particle sizes for one experiment during the detonation of TNT charge of 40 mm in diameter.

Figure 9. Dynamics of the average size of nanoparticles for all experiments during the detonation of TNT charge of 30 mm in diameter.

The dynamics of nanoparticle sizes obtained under the following assumptions. The scattering centers are a sphere with uniform density (excluding the phase state). Carbon in the diamond form gives more intensive SAXS signal. Replacement of real radiation spectrum to
Figure 8. Average size of carbon particle versus time in detonation of a cylindrical TNT charge of 40 mm diameter: 1 – experimental data, 2 – smooth spline.

Figure 9. Average size of carbon particle versus time in detonation of a cylindrical TNT charge of 30 mm diameter: 1 – experimental data, 2 – smooth spline.

A monochromatic, as shown previously does not lead to large error. Replacement the size distribution of nanoparticles by average size introduces the greatest error in mind a very strong dependence of the SAXS intensity from the particle size. Therefore, further efforts will be made to determine the size distribution of the scattering centers.

4. Conclusions
The SAXS dynamics in detonation of cast TNT charges (of different diameter) was measured. Dynamics of the average size of the condensed carbon nanoparticles behind a chemical reaction zone recovered from SAXS distributions in the Guinier approximation. The minimal particle size registered in experiments is 2 nm. Particles of this size are registered immediately behind the detonation front. Then the average size of particles increases. We observe, that the time of nanoparticles growth behind the chemical reaction zone depends on size of initial charge. It increase with increase in diameter of charge.

The experiments do not allow us to speak about the phase state of nanoparticles. However, a further increase in the intensity of SR will enable to measure the diffraction at large angles, and, consequently, to determine the phase composition of condensed carbon in the detonation products.

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References
[1] Tarver C M, Kury J W and Breithaupt R D 1997 Journal of Applied Physics 82 3771–82 URL http://scitation.aip.org/content/aip/journal/jap/82/8/10.1063/1.365739
[2] Grebenkin K, Taranik M and Zherebtsov A 2006 Proc. 13th International Detonation Symposium 496–505
[3] Aleshchev A N, Zubkov P I, Kulipanov G N, Lukyanovich L A, Lyakhov N Z, Mishnev S I, Ten K A, Titov V M, Tolochko B P, Fedotov M G and Sheromov M A 2001 Combustion, Explosion, and Shock Waves 37 585–93
[4] Evdokov O, Fedotov M, Kulipanov G, Luckjanovich L, Lyakhov N, Mishnev S, Sharafutdinov M, Sheromov M, Ten K, Titov V, Tolochko B and Zubkov P 2001 Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 470
[5] Titov V, Tolochko B, Ten K, Lukyanchikov L and Pruuel E 2007 *Diamond and Related Materials* 16 2009–13 ISSN 0925-9635 proceedings of the Joint International Conference: Nanocarbon and Nanodiamond 2006 URL http://www.sciencedirect.com/science/article/pii/S0925963507003810

[6] Ten K A, Titov V M, Pruuel E R, Kashkarov A O, Tolochko B P, Aminov Y A, Loboyko B G, Muzyrya A K and Smirnov E B 2014 *Proc. 15th International Detonation Symposium* 369–74

[7] Titov V M, Pruuel E R, Ten K A, Lukyanchikov L A, Merzhievskii L A, Tolochko B P, Zhulanov V V and Shekhtman L I 2011 *Combustion, Explosion, and Shock Waves* 47 3–15

[8] Pruuel E R, Ten K A, Tolochko B P, Merzhievskii L A, Lukyanchikov L A, Aulchenko V M, Zhulanov V V, Shekhtman L I and Titov V M 2013 *Doklady Physics* 58 24–8

[9] Bagge-Hansen M, Lauderbach L, Hodgin R, Bastea S, Fried L, Jones A, van Buuren T, Hansen D, Benterou J, May C, Graber T, Jensen B J, Ilavsky J and Willey T M 2015 *Journal of Applied Physics* 117 245902 URL http://scitation.aip.org/content/aip/journal/jap/117/24/10.1063/1.4922866

[10] Shekhtman L I, Aulchenko V M, Bondar A E, Dolgov A D, Kudryavtsev V N, Nikolenko D M, Papushev P A, Pruuel E R, Rachek I A, Ten K A, Titov V M, Tolochko B P, Zhilich V N and Zhulanov V V 2012 *Journal of Instrumentation* 7 C03021 URL http://stacks.iop.org/1748-0221/7/i=03/a=C03021

[11] Feigin L A and Svergun D I 1987 *Structure Analysis by Small-Angle X-Ray and Neutron Scattering* (NY, Plenum Press.)

[12] Schnablegger H and Singh Y 2013 *The SAXS Guide* (Anton Paar GmbH)