Study of the dynamics of nanoparticle sizes in trinitrotoluene detonation using the VEPP-4M synchrotron radiation

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Abstract. Here we present experimental data on measuring condensed carbon nanoparticle sizes in trinitrotoluene (TNT) detonation. Nanoparticle sizes were determined from measured distributions of small-angle x-ray scattering (SAXS). The work was carried out at the VEPP-4M (BINP) accelerator complex. In this work, we also carried out a SAXS simulation with a real spectrum on the SYRAFEEMA (Synchrotron Radiation Facility for Exploring Energetic Materials) station (wiggler radiation, TNT absorption, absorption of the DIMEX-3 detector). Comparison of the calculated and measured SAXS distribution allows one to obtain the dynamics of the average sizes of carbon nanoparticles behind the detonation front using a pink synchrotron radiation (SR) beam. The measured particle sizes in the chemical reaction zone are $\approx 2$ nm. Carbon nanoparticles with a maximum size of $\approx 4$–$5$ nm are found outside the chemical reaction zone.

1. Introduction

In the early 2000s, researchers of the Institute of Hydrodynamics and the Institute of Nuclear physics began to develop a new technique to study fast processes using high-energy accelerators [1]. The high intensity of SR allowed recording the dynamics of diffractive scattering with an exposure of 1 ns. The SAXS intensity depends on electron density fluctuations due to carbon condensation in detonation of oxygen-deficient high explosives [2–6].

A new experimental station for studying fast processes was launched in 2015. The SYRAFEEMA station using SR from the VEPP-4M accelerator complex has much higher radiation intensity than the similar station “Extreme States of Matter” using SR from the VEPP-3 accelerator complex, which allows x-ray examination of explosive charges of larger diameter. This new station allows an increase in the mass of the charges studied by a factor of 10—to 200 g [7, 8].

Similar experiments have been conducted at the Advanced Photon Source (Argonne National Laboratory, United States). These studies have shown hexanitrostilbene detonation produces carbon particles with a radius of gyration of 2.7 nm, which corresponds to the 7 nm diameter of spherical particles, which is recorded in 400 ns and remains constant for several microseconds. Their charges are very small, about 500 mg [9].
In this paper, we present data on particle size dynamics in TNT detonation. The study of TNT is important as this explosive is the main component of mixtures used in the commercial production of ultrafine diamonds.

2. SAXS simulation
A feature of the SYRAFEEMA experimental station located on the VEPP-4M beam line 8 is the use of a 7-pole wiggler, whose radiation spectrum is shown in figure 1.

As an SR beam passes through an explosive charge, part of the radiation is absorbed. The attenuation of the x-rays passing through a material (of density $\rho$ and thickness $d$) is determined using the mass absorption coefficient $\mu/\rho$ shown in figure 2. In the modeling, we used typical values for the cylindrical TNT charge studied: $\rho = 1.6$ g/cc and $d = 40$ mm. The intensity of the attenuated radiation is given by the formula

$$I = I_0 \exp(-\frac{\mu}{\rho} \rho d).$$

In the experiments, SAXS was recorded with a DIMEX-3 detector, which consists of a gas ionization chamber coupled with an electronic amplifier. The detector was filled with a mixture of Xe-CO$_2$ (80–20%) at a pressure of 7 bar. The efficiency of photon detection as a function of the energy is shown in figure 3 [10].

Thus, the real spectrum of SR at the station is the sum of the wiggler emission spectrum (figure 1), the absorption spectrum of the charge (figure 2), and the detection efficiency of the DIMEX-3 detector (figure 3) and is shown in figure 4.

The SAXS intensity from a spherical particle as a function of the scattering angle ($2\theta$) is proportional to the form factor $P(q, R)$ defined by the formula

$$P(q, R) = \left[\frac{\sin(qR) - (qR)\cos(qR)}{(qR)^3}\right]^2,$$

where $q = 4\pi \sin(\theta)/\lambda$ is the scattering vector, $R$ is the radius of the spherical particle and $\lambda$ is the scattered radiation wavelength [11, 12].

The sizes of the scattering centers were determined using the Guinier approximation—$I(q, R) \sim \exp(-q^2 R_g^2/3)$, where $R_g$ is the radius of gyration of the particle. For a spherical homogeneous particle of radius $R$, $R_g = \sqrt{3/5}R$.

Taking the logarithm of the intensity $\ln(I(q, R)) = \ln(I_0) - q^2 R_g^2/5$, we obtain a function which decreases linearly from $q^2$ and from whose slope $w$ we can determine the size of the spherical particle $2R = 2\sqrt{-5w}$ [11, 12].

We have developed a program to calculate the SAXS with consideration of the energy spectrum from particles of different diameters. The results of such calculations are shown in figure 5. It can be seen that different slopes of the SAXS signal correspond to different diameters. Thus, the SAXS from the pink SR beam allows us to retrieve information on particle sizes.

The effective photon energy was determined by the least squares method so that the deviation between the SAXS signal with the real spectrum and the SAXS with the effective energy was minimal within the intensity decay half-time. Thus, we obtained effective x-ray energy of 39 keV (figure 6). At this energy, the SR wavelength is $\lambda = hc/E = 0.0318$ nm. By the effective energy is meant the monochromatic radiation energy that most closely describes the SAXS from the real spectrum at the station.

Having determined the effective energy, we can introduce the concept of the scattering vector $q = 4\pi \sin(\theta)/\lambda$ for the radiation spectrum and determine the particle size using the Guinier formula.
Figure 1. Spectrum of the SR from the VEPP-4 wiggler.

Figure 2. Mass absorption coefficient for TNT.

Figure 3. Detection efficiency of the detector for photons of different energy.

Figure 4. Real radiation spectrum at the SYRAFEEMA station.

Figure 5. SAXS for spherical particles of different sizes with consideration of the real spectrum.

Figure 6. SAXS with consideration of the spectrum and effective energy.
3. SAXS measurement experiments

The SAXS measurements were carried out on the VEPP-4M beam line 8. The experimental setup is described in [4–6]. SAXS was recorded with a DIMEX-3 detector with an angular resolution of $3 \times 10^{-5}$ rad, located at 3432 mm from the explosive charge. The time between the frames was 600 ns. A schematic of the experiment is shown in figure 7.

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/cc.

Ultradispersed diamonds (UDD) (Altai scientific and production center, Biysk) with a known size of $\approx 4$ nm were used for calibration. SAXS from the UDD is shown in figures 8 and 10. Experimental SAXS distributions are presented in figure 9. Using the Guinier approximation (figure 11), we obtained the dynamics of condensed carbon nanoparticle sizes in TNT detonation, which is shown in figure 12.

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 SAXS signal. Replacement of real radiation spectrum to 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 distribution of the scattering centers in size.
Figure 10. SAXS from UDD, Guinier approximation.

Figure 11. SAXS in TNT detonation at 4.2 µs behind the front, Guinier approximation.

Figure 12. Average particle size of carbon versus time in detonation of a cylindrical TNT charge of 40 mm diameter.

4. Conclusions
The SAXS dynamics in detonation of cast TNT charges was measured. The dynamics of the average sizes of carbon nanoparticles behind the detonation front was obtained by comparing the calculated and measured SAXS distributions. The minimum particle size detected in the experiment was 2 nm. Particles of this size were detected in 0.5 µs; then the average size increased within 4 µs and reached 4–5 nm. These experiments do not provide information on the phase state of nanoparticles, but further increase in the SR intensity will make it possible to measure large-angle diffraction and, therefore, determine the phase composition.
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