Where and when are nanodiamonds formed under explosion?

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Abstract

The formation of nano-sized diamonds during the detonation of a TNT/RDX explosive with 50/50 composition was investigated experimentally *in situ* by means of small-angle X-ray scattering using synchrotron radiation with nanosecond time resolution. No nanodiamonds were observed immediately after the detonation front, as only the nucleation of nanodiamonds takes place at this moment. The increase in small-angle X-ray scattering which was observed during 2 μs was the cause of the dynamic growth of nanodiamonds. The inclusion of a very thin shell around the explosive causes a significant increase in this time, because the kinetic of nanodiamonds growth was changed.

In another set of experiments, the nanodiamonds were artificially introduced into different explosives before explosion. The nanodiamonds were not destroyed in RDX immediately after the detonation front, but burned in an oxidants with some delay. In TNT, the nanodiamonds were not destroyed at all.

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1. Introduction

Although a rather large number of works deal with the synthesis of nano-sized diamonds (ND) during explosion [1], the problem of their formation and the more general questions concerning the condensation of carbon during the detonation of explosives with a negative oxygen balance remain controversial. An answer to this question is important both for understanding the physical nature of this phenomenon and for estimations of the amount of energy liberated during the exothermal coagulation of carbon clusters. The first investigation performed from the point of view of such an energy-related approach was published in 1987 [2]. The calculations performed in this work suggested an overall addition of 10% to the amount of energy liberated in the detonation process itself in order to form nano diamonds.

The first results dealing with the formation of nano-sized diamonds produced during explosion were reported in 1989 [3].

It was assumed that the synthesis process was determined mainly by the zone of chemical reaction based on the constant particle size distribution of nano-diamonds in the purified products (conserved after explosion) for different explosive sizes. It is evident that only the processes in the zone of the chemical reaction remain unchanged. Correspondingly, the time of synthesis was estimated to be several tenths of a microsecond (not more than 0.5 μs) [3]. In order to adjust the calculated data to fit the experimental results, Ershov [4] supplemented the model [2] with an *a priori* limitation of particle size. The time of growth estimated in this way was in good agreement with the estimation of synthesis time proposed by Titov [3].

The calculated data were compared to the experimental results of the launching of very thin metal plates by detonation products (DP) formed from explosives with a negative oxygen balance [5]. It was revealed that this process is more accurately described if one assumes that the condensation of carbon proceeds outside the chemical reaction zone, or, in terms of the detonation theory, beyond the Chapman–Jouguet plane which separates the reaction zone from the gas dynamic flow of DP.

In the very first application of synchrotron radiation (SR) to the investigation of detonation processes, it was established that the signal of small angle X-ray scattering (SAXS) of the SR
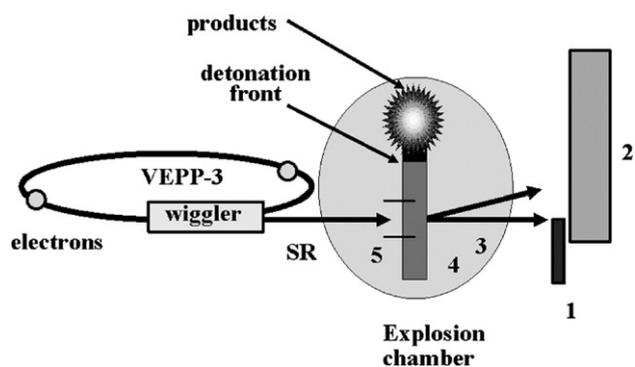
Fig. 1. The setup for in situ SAXS experiments: 1 — beam stop, 2 — SAXS one-coordinate DIMEX detector, 3 — SR scattered and transmitted beams, 4 — explosive, 5 — wire contact detector for synchronization of DIMEX and explosion.

grows relatively slowly, taking 1–1.5 μs for an explosive size of 10–15 mm [6]. It was assumed on this basis that the formation of carbon particles (including nano-sized diamonds) occurs outside the zone of chemical reaction (in this case, its length is about 0.7 mm). This conclusion caused several critical comments [7], which can be reduced to the following considerations. In the SAXS procedure, the intensity of the scattered signal is (as the first approximation) proportional to the squared difference between the densities of the scattering particle and that of the medium in (1).

During the initial moment of detonation, the SAXS signals of DP and ND, the densities of which are about 2 g/cm^3 and 3 g/cm^3, may be unnoticeable to the detector. During rarefaction of DP with a decrease in the DP density, the SAXS signal will become observable. This may also explain a trend to increase the time of the SAXS signal maximum with an increase in the exploding charge diameter [8], because DP rarefaction will take more time in this case.

In a previous paper, we described a novel approach to the problem [8]. This paper showed that carbon condensation (including the synthesis of nanodiamonds) behind the front of the detonation wave should necessarily take into account rarefaction waves from the side surface of a real explosive, that is, a three-dimensional formulation is involved (in the case of a cylindrical charge). Such a consideration allowed us to build [8] a hypothetical model of the phenomenon which was in agreement with the experimental data. In essence, this was the first work in which researchers rejected the classical one-dimensional formulation for the analysis of the process.

This brief review should mention works [9,10] where the authors determine a position of nanodiamond synthesis on the (P–T) diagram of carbon, taking into account the size of the nanoparticles. However, this analysis was carried out in a one-dimensional formulation.

As demonstrated above, the published works on the synthesis of nano-diamonds show the existence of different points of view on the process. The goal of this paper is to present results which will help to understand the phenomenon of the formation of nanodiamonds by detonation.

2. Experimental results

2.1. In situ SAXS experiment

In this work, the synchrotron radiation (SR) from the wiggler with a 2T field VEPP-3 electron accelerator (Institute of Nuclear Physics of Siberian Branch of Russian Academy of Science) was used with the following parameters: single bunch mode at $E=2$ GeV, $I=150$ mA (Fig. 1).

We reported earlier about SAXS signals detected during the explosion of different materials [6,8]. Here, we describe SAXS experiments (Fig. 1) using a Detector for Imaging of Explosions (DIMEX) and discuss the time variation of the SAXS signals during the explosion. The composite explosive trinitrotoluene–hexogen (TNT/RDX) was used in a 50/50 ratio in a cylindrical form with a diameter of 15 mm. Charges were placed in an explosion chamber and positioned for appropriate exposure to SR. The scattered radiation was recorded with a gas detector
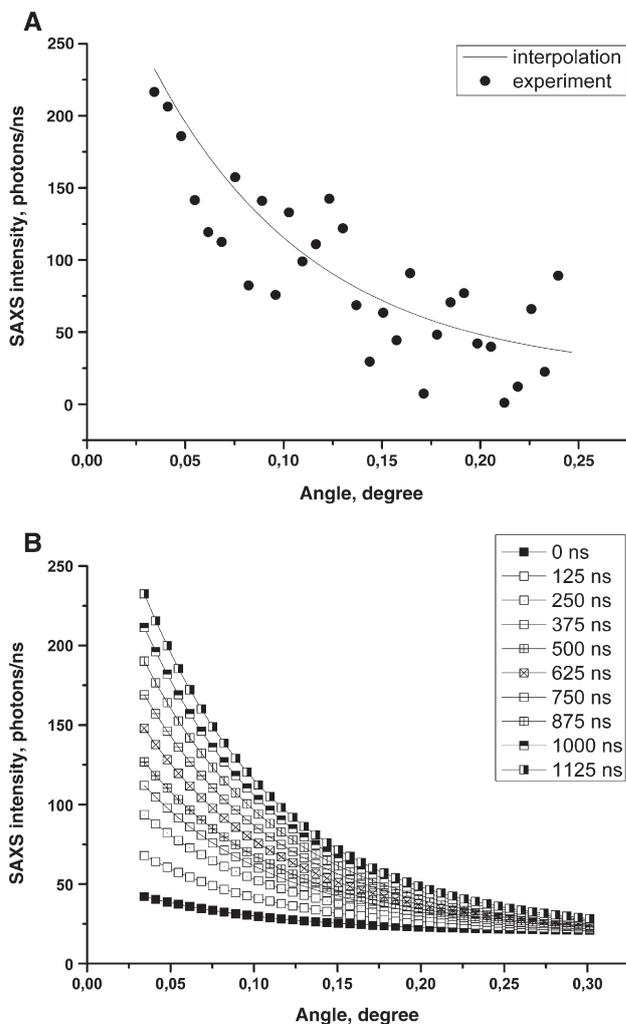
Fig. 2. Small angle X-ray scattering experimental data of TNT/RDX (50/50) during explosion. A) Experimental SAXS data (and interpolation curve) at the moment $t=1125$ ns after the passing of the detonation front. B) The same interpolated curve and a previous one from the beginning of detonation. Each frame was captured with an exposure time of 1 ns and a periodicity of 125 ns.

Fig. 5. The time-derivate integral SAXS signal versus muff thickness. Muffs causes a deceleration of diamonds formation.

second; 3 and 6 mm thick shells caused a decrease to $2.4*10^{12}$ and $1.5*10^{12}$ pulses per second, respectively.

Taking into account the additional absorption of the primary SR beam and scattered radiation (SAXS) by the presence of a shell, a correction was made for the curves of SAXS dependence on time. The absorption of 20 keV X-rays for 1.5, 3 and 6 mm thick shells are 10%, 19% and 34%, respectively. The corrected dependence of the derivative dI/dt on time is shown in Fig. 4.

Hence, it was demonstrated experimentally that a delay in DP rarefaction conditions causes a deceleration of the process of nano-diamond formation.

The experimental curve dI/dt *versus* the shell thickness can be extrapolated into the region of large thickness values (Fig. 5). The extrapolated curve crosses the abscissa axis at about 15 mm. Therefore, it may be concluded that with a shell thickness of about 15 mm, nano-diamonds would not be formed. Such a formal conclusion has a specific physical explanation: the presence of a shell causes a shift in the DP rarefaction front, and it therefore brings the nano-diamond formation region away from the detonation front at a distance comparable with the exploding charge diameter.

The maximum of $D_N(r)$ was near 5 nm with a half-width of 1 nm. Very small increases in these parameters were observed during explosion in these experiments.

2.3. Internal diamond labels

All these experiments were carried out with pressed exploding charges 15 mm in diameter and about 80 mm long. Initiation was carried out with a plane wave generator.

In the *in situ* SAXS experiments, three types of explosive compositions were used: 1) TNT+8% ND, 2) TNT/RDX 50/50, 3) RDX+8% ND (mass).

The second composition is the one used in the industrial production of ND; TNT yields a notably smaller amount of nano-diamonds but a larger amount of carbon residue; RDX, a more powerful explosive, has zero oxygen balance and leaves no residue. The 8% ND added in charges 1 and 3 corresponds to the amount of ND formation during the explosion of TNT/RDX

50/50. Therefore, charges 1 and 3 are model systems for the nucleation of 8% ND in TNT/RDX 50/50 during detonation.

The results are shown in Fig. 6. Time $t=0$ is the moment when the detonation wave reaches the plane of the SR beam. A decrease in the SAXS signal at this moment on curves 1 and 3 corresponds to an increase in the density ρ_2 of the explosive at the front of the detonation wave, and consequently there is an increase in the absorption of SR and a decrease in contrast in (1). No change in diamond volume fraction φ_1 was observed at this moment. The integral SAXS signal from TNT after a sharp decrease at the detonation front was recovered, and it started to increase due to rarefaction and formation of condensed carbon, and as a consequence contrast $(\rho_1 - \rho_2)$ and φ_1 increased thereafter.

During the detonation of the powerful explosive RDX with oxygen in the DP, no ND were destroyed at the detonation front ($t=0$), but a substantial portion of small nanodiamonds was burned in the time interval $t=0-1$ μs, during which φ_1 decreased and the integral SAXS intensity decreased.

Curve 2 corresponds to the integral intensity of TNT/RDX 50/50. The signal starts from the zero point (0,0) when time $t=0$ and intensity $I=0$, and increases smoothly, almost repeating the shape of curve 1, but shifting at a lower value. It reaches the same intensity as curve 1, but with a time delay. Due to special measures, the accuracy of different experiments at the zero point was not worse than 100 ns. A phase shift between curves 1 and 2 at the same level of intensity is always much greater than this value. These two curves should start from the same point A in Fig. 6 if the assumption about nano-diamond formation in the zone of the chemical reaction ($\tau \sim 130$ ns [11]) is right. Instead, curve 2 did not start from point A (Fig. 6), and the amount of diamond nucleated during 100 ns in the detonation wave did not reach 8%.

This experiment proved the following: a) nano-diamond particles are quite reliably recorded by SAXS if the density of the environment is close to the density of the explosive (~ 1.6 g/cm^3); b) the SAXS signal related to the growth of particles from the TNT/RDX mixture is noticeably delayed versus the SAXS
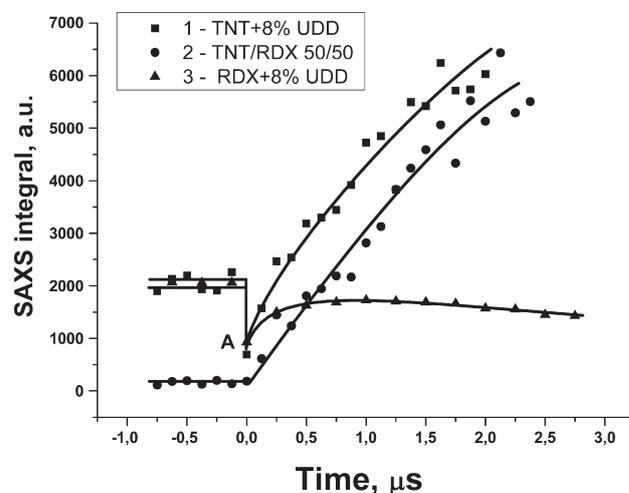
Fig. 6. SAXS behavior versus time during explosion: (1) — from composite explosive TNT+8% nanodiamonds; (2) — from TNT/RDX; (3) — from composite explosive RDX+8% nanodiamonds.
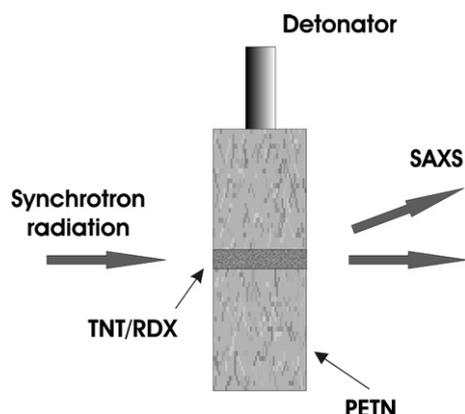
Fig. 7. Composite explosives: the diamond generating part was made from a TNT/RDX (50/50) 2 mm length disc, and the two parts not generating diamonds was made from PETN. When narrow SR beam irradiated lower boundary PETN-TNT/RDX, the disc was shifted down ∼1 mm by the detonation front pressure and then irradiated by SR. The reaction zone of TNT/RDX produced a very weak SAXS signal at this moment.

of nano-diamond particles introduced preliminarily in TNT; c) the nano-diamonds are not formed in the detonation wave.

2.4. Localization of ND area nucleation

Charges were made of a penthaerythritol tetranitrate (PETN) explosive with a zero oxygen balance; hence we would expect that no ND would be produced and no SAXS would be recorded during detonation. The PETN has parameters close to those of TND/RDX in the Chapmen-Jouguet plane ($P = 250$ kbar), and the mass velocities are also approximately equal. A disc with a thickness of 2 mm made from TNT/RDX 50/50 was inserted coaxially between 2 cylinders made from PETN (Fig. 7). The disc was used as a generator of ND growth in this local area. There were no ND from other parts of the charge during this experiment.

The ND were nucleated in the disc and then spread around. The space near the boundary PETN-TNT/RDX charge was scanned by SR beams. It was necessary to do more than a dozen explosions for the scanning experiment: one explosion for each position of the SR beam from TNT/RDX-PETN boundary. A SAXS signal was generated if scattering of ND took place. There was no SAXS from areas free of TNT/RDX 1 μs after the detonation front passed.

The zone of chemical reaction for TNT/RDX 50/50 does not exceed 0.7 mm [11], and the time of reaction does not exceed $\tau \sim 130$ ns in this zone. This zone was shifted down in our experiment by detonation wave pressure (Fig. 7). In one position

of the SR beam when it irradiated the area under the disc, the reaction zone was shifted from to the bottom part of the disk. Therefore, we expected SAXS to respond if all ND were nucleated during this time in the reaction zone. In the experiment, however, the reaction zone gives very weak SAXS signals, which also demonstrates that the generation of diamonds occurs behind the zone of chemical reaction in the PD.

3. Conclusions

The theories of detonation diamond formation [4,7] are based on the suggestion [3] that condensation of carbon occurs in zone of the chemical reaction. However, no *in situ* experiments have confirmed this suggestion. This publication proves, along with similar real-time experiments [5,8], that condensation occurs outside of the zone of the chemical reaction. The hypothetical model [8] that diamonds may be formed during unloading at a substantial distance from the detonation front has been confirmed experimentally. Consequently, existing theories need correction, which demonstrates the importance of these new experimental results for our understanding of the fundamental principles of diamond nucleation.

Acknowledgements

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