Invetigation of Micro-, Meso-, and Macrostructure of the Pressed Parts Made of HE TATB

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Abstract. The molecular structure of individual explosives was studied with the help of diffraction methods (XRD) including the case with the varying initial conditions. The small angle X-ray scattering method (SAXS) was used to study the structure (porosity) in the range of 1-10 nm. The structure with the size ranging from 0.001-10 mm was studied with the help of the X-ray computer microtomography (XRCT). The data on the morphology of the HE structure inhomogenuities were gathered with the help of the electron (EMS) and optical microscopy (OMS).

Introduction

The present-day understanding states that a heterogeneous explosive transformation into explosion products begins at the front of the initiating shock wave according to the homogeneous mechanism and continues behind the front according to the local-thermal mechanism [1, 2]. It is assumed that regularities in decomposition of an explosive material (HE) at the wave front depend on its molecular and intermolecular structures with their characteristic sizes being within the subnanometer area. A share of an explosive decomposed at the front decreases with the external action intensity. And the role of the local-thermal mechanism simultaneously grows in the process of initiation. In addition, the shock wave induces local elevated temperatures – hot spots – on inhomogeneities of the micro-, meso-, and macrostructure (inside HE) due to energy dissipation. Elevated temperatures create favorable conditions for the chemical reaction to commence in heated up areas and to propagate to the surrounding substance. Different mechanisms are discussed in publications as possible reasons of heat localization. But intricacy of the phenomenon of explosive transformation initiation prevents us from focusing on one of them. By no means unimportant is that changes in loading conditions can induce changes in mechanisms whose

combined action predetermines the initiation process.

Nowadays, phenomenological models of HE decomposition kinetics are widely used. These models are based on the quantitative interrelation between the structure inhomogeneities and the experimentally determined sensitivity of explosives to external stimuli. Without going into details of mechanisms themselves, it is assumed that there is interrelation between the inhomogeneity size, i.e. a pore size, and energy accumulated in this pore due to compression. The fact that heat removal is proportional to the surface area of a heated pore is also taken into account. The mathematical model of HE decomposition kinetics, which is constructed based on these assumptions, strongly needs actual data on the inhomogeneities distribution inside an explosive material. Verification of these models requires empirical data both on the molecular structure of HE and on the heterogeneous structure of an HE charge. In its turn, the heterogeneous structure depends on the fabrication process and undergoes changes at mechanical and thermal impacts on HE. The whole of inhomogeneities in the HE charge structure can be conventionally subdivided into intracrystalline (1-100 nm), intragranular (0.1-100 μm), and intergranular (0.1-10 mm) classes. Therefore, in order to construct the physical model of HE decomposition kinetics, we need information on the structure in the range from the molecular structure with characteristic sizes of about 10^{-10} m to the HE macrostructure with characteristic sizes up to 10^{-2} m.

Results

In these investigations, the structure of heterogeneous explosives was studied with the help of methods given in Fig. 1.

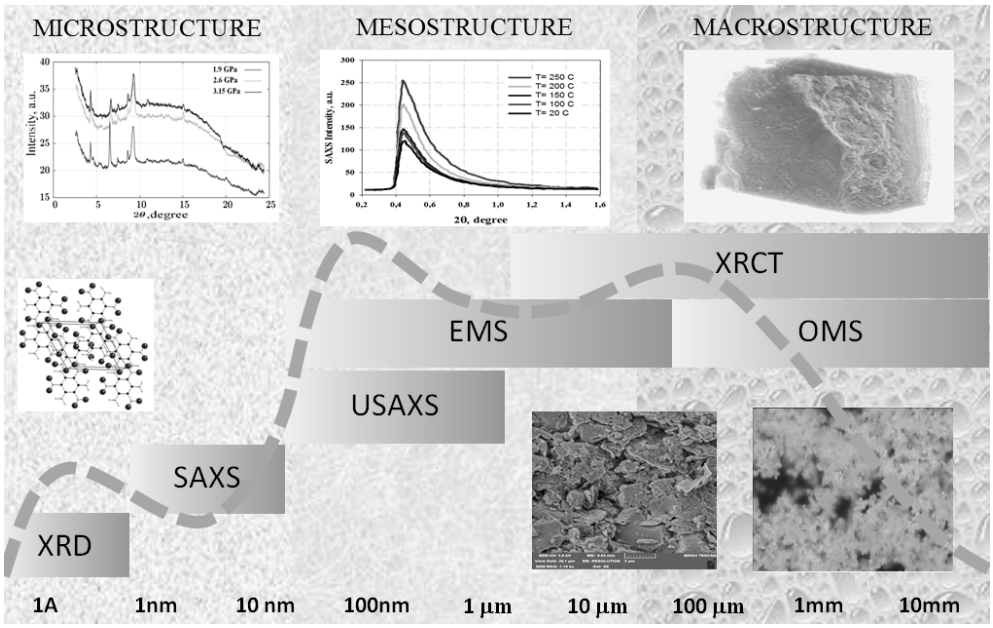

Fig. 1. Methods used to study structure of explosives.

Our investigations covered a wide range of structure changes from units of Angstrem up to millimeters. The molecular structure of individual explosives was studied with the help of diffraction methods (XRD) including the case with the varying initial conditions (temperature and pressure applied to explosives). The small angle X-ray scattering method (SAXS) was used to study the structure (porosity) in the range of 1-10 nm. The structure with the size ranging from

0.001-10 mm was studied with the help of the X-ray computer microtomography (XRCT). Sizes in the range from 0.01 to 1 μm can be studied with the help of the ultra small angle X-ray scattering method (USAXS). The data on the morphology of the HE structure inhomogenuities were gathered with the help of the electron (EMS) and optical microscopy (OMS).

The applied XRD, SAXS, and XRTC methods use a monochromatic beam of synchrotron radiation (SR) from an electron-positron collider. The application of synchrotron radiation makes it possible to achieve high levels of X-ray exposure within a short period of time and allows continuous recording of physical-and-chemical phenomena in a real-time mode. Small angle divergence of synchrotron radiation makes this radiation critically important for precision measurements. Lawrence Livermore National Laboratory was the pioneer to use synchrotron radiation for the internal HE structure investigation [3, 4]. Argonne National Laboratory used Advanced Photon Source to gather the data on initial structure of LX-17 [4, 5]. In our country, synchrotron radiation was first used for these purposes on VEPP-3 accelerator at the Institute of Nuclear Physics, RAS Siberian Branch. On this accelerator, the source of synchrotron radiation is a wiggler having the field of 2 T. The synchrotron radiation of this wiggler has the continuum spectrum with critical wavelength of λ_c= 2.33 Å and total power of 10^3 W.

This paper gives results of investigating the structure of TATB (1,3,5-triamino-2,4,6-trinitrobenzene). Taken alone and in combination with plasticizers, this HE is of great scientific interest due to its exclusively low sensitivity to external stimuli (both heat and shock). At the same time, it is extremely attractive in terms of scientific research because of its complex crystalline structure. TATB crystals have triclinic symmetry being a challenge for the X-ray structural analysis. While studying such materials as TATB, one should draw attention to the directed dependence of their thermal and mechanical properties because of intrinsic anisotropy of the triclinic system.

Molecular structure of an individual HE, namely TATB (typical size of 0.1-1nm), is investigated by the powder X-ray diffraction method including hydrostatic compression of the explosive in diamond anvils. Fig. 2 shows TATB diffractogram registered under normal conditions. In this figure, the radiation scattering angle is plotted along the x-axis and radiation intensity *I* (in arbitrary units) is plotted along the y-axis.

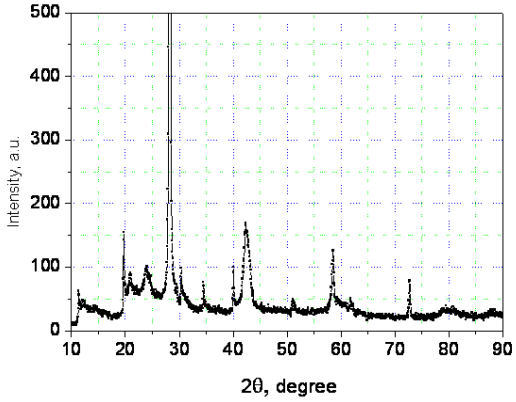

Fig. 2. TATB diffractogram registered at atmospheric pressure and T=293K. X-ray quanta energy E=8.2 keV.

The TATB unit cell sizes calculated based on the X-ray analysis during this work are in good agreement with the results given in [8]. The TATB unit cell geometry is shown in Fig. 3.

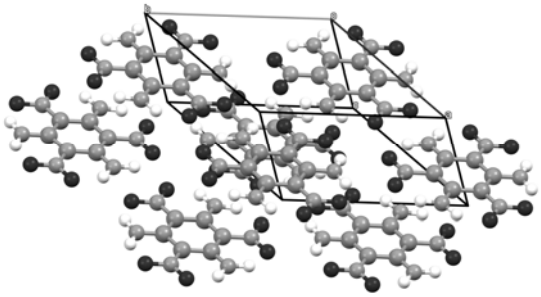

Fig. 3. TATB crystal unit cell.

Investigation of isothermal compression in combination with the data on shock adiabatic compression provide a framework for understanding and interpretation of such phenomena as phase transitions, melting under shock loading, and detonation initiation. This paper considers TATB compression approximately up to 5 GPa at T = 293K. The dffraction signal was registered using a detecting system based on

MarResearch image plate. The energy of X-ray quanta was E=33.7 keV [9].

Up to ten diffraction peaks were registered at atmospheric pressure (Fig. 2); this is quite sufficient for triclinic system analysis. However, the number of registered peaks decreased down to four peaks when the pressure grew up to 5 GPa. Fig. 4 shows TATB diffractograms for several levels of compression.

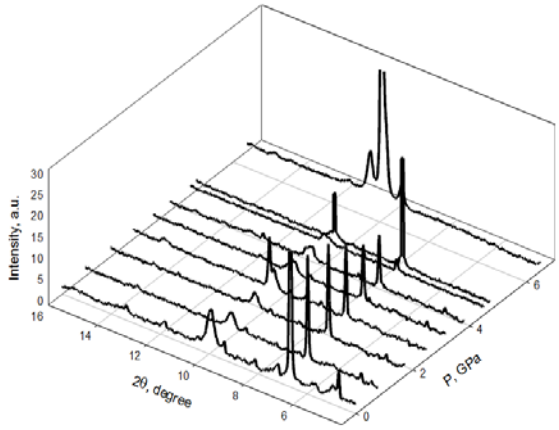

Fig. 4. TATB diffractograms for the case of isothermal compression. X-ray quanta energy E=33.7 keV.

Minimum six diffraction peaks need to be registered in order to calculate TATB unit cell parameters. For triclinic system, an assumption of TATB unit cell behavior under compression was required to decrease the number of independent variables in the solution. The differences in the molecular and intermolecular forces specify anisotropic crystalline structure of TATB. Strong hydrogen bonds are present mainly in the crystallographic *ab* plane while weak Van der Waals forces are active between different *ab* planes (Fig. 3a). Such structural features condition higher TATB compressibility along crystallographic axis *c* when compared to the *a* and *b* crystallographic axes. Therefore, in this work, the ratio between lengths of the *a* and *b* crystallographic axes was considered to be a constant value in order to simplify the crystalline structure calculation. Changes (calculated under above assumptions) in the TATB volume with the applied hydrostatic pressure are shown in Fig. 5.

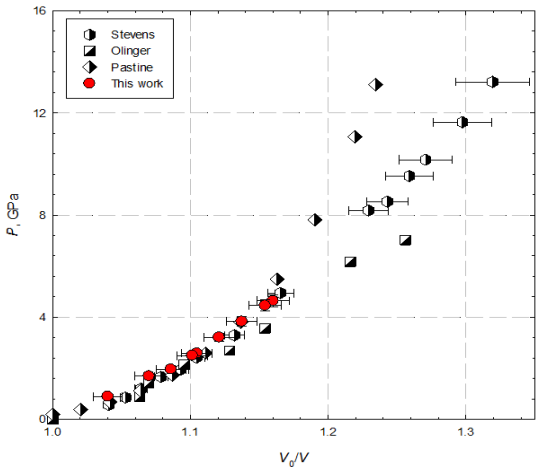

Fig. 5. Data on TATB isothermal compression.

For comparison, these data are shown along with appropriate data obtained by other researchers [8, 10, 11]. In the pressure range under study, our data agree well with the results of [8, 10]. The data on the HE isothermal compression are needed to construct the equation of state. In addition, these investigations provide valuable information on how molecular structure changes under external stimuli (pressure and temperature) including the case when they approach the critical level. For this purpose, present-day study involves wider pressure range as well as conditions of isobaric heating.

The small angle X-ray scattering method (SAXS) was used to study the structure of heterogeneous explosive charges. Generally, this method is similar to the X-ray diffraction (XRD) method except that the small angle diffraction gives information on larger-size structural inhomogeneities. Instead of scattering from atomic planes, this method registers scatter for randomly distributed air pores in the HE matrix; these pores are the primary source of small-angle scattering. Figure 6 shows profiles of the small angle SR scattering intensity for TATB with the initial porosity of ~1% at T= 293K. This figure also shows the data on SAXS intensity for TATB heated up to 250°C. The SAXS signal grows significantly with temperature.

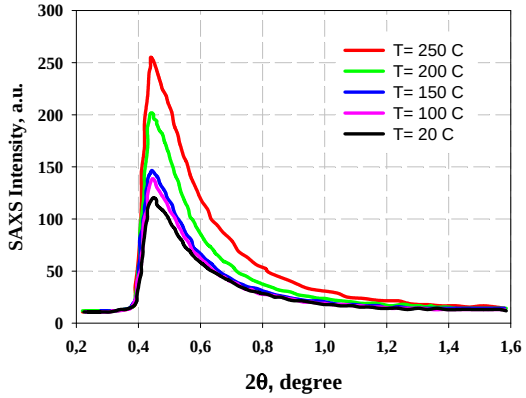

Fig. 6. SAXS distribution at different temperatures of TATB. X-ray quanta energy E=8.2 keV.

Increase in the scatter intensity can be due both to increased number of scattering particles, and also to their increased size. According to the SAXS theory [12, 13], density inhomogeneities lead to small-angle scattering of X-radiation with its intensity written as:

$$I(q) = |\Delta\rho|^2 \int_0^\infty |F(q,r)|^2 V^2(r) NP(r) dr\,, \quad (1)$$

where $q = \frac{4\pi}{\lambda}\sin(\theta)$, where λ – scattered radiation wavelength, and 2θ – scattering angle. Then, r – scattering particle radius, $\Delta\rho$ – scattering contrast associated with the difference in the density between an air pore and the HE matrix (in our case – TATB), $F(q,r)$ – scatter form-factor specified by the morphology of air pores (sphere, ellipse, etc.), $V(r)$ – particle volume, N – total number of pores, and $P(r)$ – likelihood of an air pore of the size r.

Even though this distribution gives only one scatter-intensity profile, backward transformation is not unique and requires model assumptions as for the structure. In this work, air pores are simulated with the help of the form-factor for spheres and thus there is no need in a priori assumptions on the shape how scatter sources (air pores) are distributed. The iteration method of successive approximations was used to determine the distribution further fitted to correspond to the measured profile of scattering in the best way provided entropy of inhomogeneities distribution is a maximum one [14].

The pore size distribution for TATB at different temperatures is shown in Fig. 7. The air pore size registered in our experiments using the SAXS method falls within the range from 1 nm to 20 nm. Analysis of the data given in Fig. 7 demonstrates the uniform increase of air pores within the entire range of sizes (from 2 nm to 20 nm) with the temperature increase up to 250°C. Specific features of pore size distribution at 200°C need to be additionally confirmed. Sizes in the range from 10 nm to 1 μm will be studied with the help of the ultra small angle X-ray scattering method (USAXS) being currently developed.

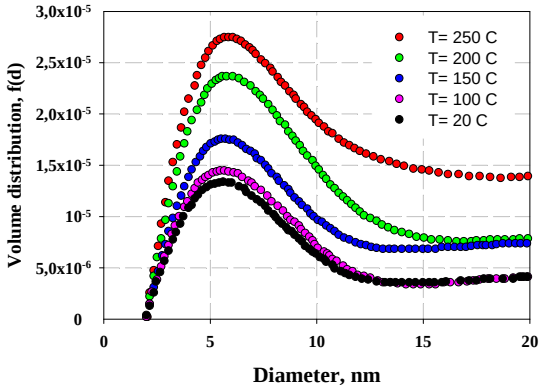

Fig. 7. Curve of pore size distribution at different temperatures of TATB.

Structural features in the 1μm – 10mm range were studied by means of X-ray computer microtomography that uses the synchrotron radiation (XRCT) [6, 7]. Figure 8 shows a 3D image of the TATB sample. This image was registered with the help of the monochromatic synchrotron radiation generated by VEPP-3 accelerator.

Summing-up of 180 projections obtained through rotation of the test sample in the vertical-axis goniometer gave the three-dimensional image [7]. A lens based on the principle of Bragg diffraction [15] from the asymmetrically slashed crystals was used to enhance spatial resolution of the method. This lens allowed the 20-fold magnified image in the x-ray range with the spatial resolution not worse than 1-2 μm. Bragg crystals help to make particulars at the media boundaries more distinct due to X-ray refraction in the test sample. Refraction contrast allows us to register

high-contrast images of objects, which is impossible in the X-ray range.

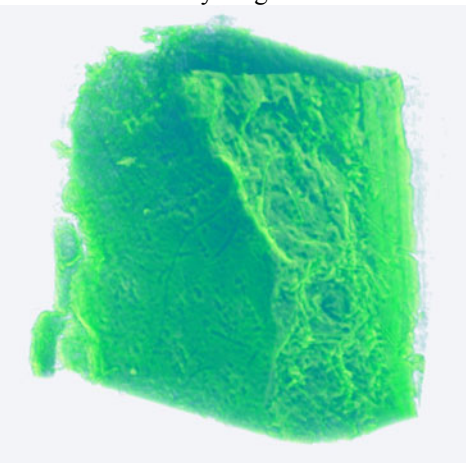

Fig. 8. 3D image of the TATB sample with 1% porosity.

Figure 9 demonstrates the curve of pore size distribution in the TATB sample with 1% porosity; this curve was obtained by processing of the computer tomographic image [6, 7].

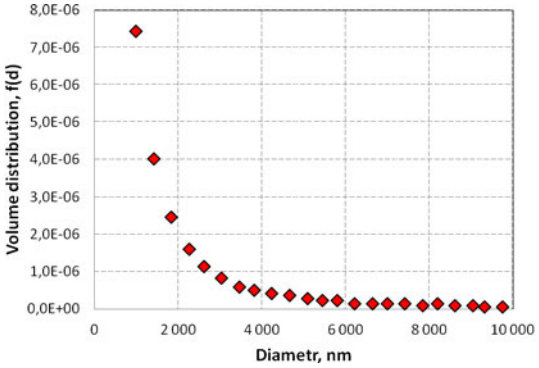

Fig. 9. Curve of pore size distribution in the TATB sample with 1% porosity.

In order to gather quantitative data on the inhomogeneities distribution from the small and supersmall angle X-ray scattering results, we need information on actual topology of air inclusions inside an explosive material. As is described above, air pores distribution is reconstructed in the assumption that these pores are spherical and this is scarcely probable due to directional pressing of HE parts. The raster electron (EMS) and optical microscopy (OMS) revealed the morphology of gas inclusions to be close to a compressed sphere with the 3/5compression coefficient. Figure 10 shows raster electron microscopy results. The EMS and OMS methods helped to determine, first, the shape, and also sizes of inhomogeneities in HE in the range from 100 nm to 10 μm. The shape of particles with the size below 100 nm needs further investigations.

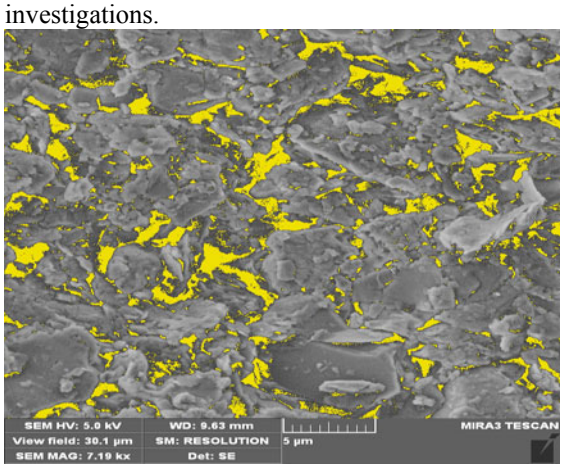

Fig. 10. EMS image.

Figure 11 shows both the summary data given by different methods that use synchrotron radiation, and also the data from paper [4] for comparison. Good agreement between results of different methods is obvious. The USAXS method will allow investigations of the area where the structure size ranges from 20 nm to 1 μm.

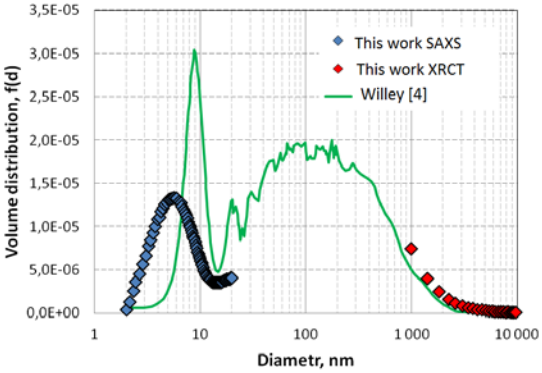

Fig. 11. Curve of pore size distribution in TATB.

Conclusions

The structure of a heterogeneous explosive material was subjected to nondestructive testing and results of this investigation are presented. Data

on the HE molecular structure ranging from characteristic sizes of about 10^{-10} m up to 10^{-2} m (macrostructure) are obtained. Investigations provided quantitative characteristics for the structure morphology of the test heterogeneous TATB including the case with different initial pressures and temperatures. Data on HE structure together with the data on HE sensitivity will help to determine effect of inhomogeneities and their amount on the initiation process and to determine mechanisms of heat localization under external stimuli on HE. The obtained data are intended to construct mathematical models for decomposition kinetics of condensed heterogeneous explosives.

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