Formation of Carbon Nets in Detonation Products of High Explosives

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Abstract. The condensation process of free carbon in the detonation products (DP) of carbon-rich high explosives was studied using the molecular dynamics method. It was shown that, if the carbon volume fraction is high enough, the carbon clusters form the net spatial structures of mesoscopic sizes bridging the opposite sides of the simulation region. The conductivity of DP was calculated considering the carbon nets as main conductors.

Introduction

Many explosives such as RDX (cyclotrimethylene-trinitramine, or hexogen), HMX (cyclotetramethylene-tetranitramine, or octogen), PETN (pentaerythritol tetranitrate), TNT (trinitrotoluene) contain carbon in excess. The carbon condensation influences some macrocharacteristics of the detonation products (DP). For example, the part of the energy release due to carbon condensation at the detonation of explosives such as TNT and triaminotrinitrobenzol is from 10 to 30 percent (depending on the theory used) that should be taken into account at composing the equations of state of explosives and inert substances. The weight fraction of the condensed carbon in the DP can be up to 20 percent. B. Hayes [1, 2] was the first who supposed the correlation between the free carbon fraction in DP (at the Chapman – Jouguet plane) and the DP conductivity (1967) but there was no convincing evidence of the exclusive role of carbon in the DP conductivity of high explosives.

He had put forward the idea of condensation of the free carbon to the connected spatial nets that serve as the conducting wires. This idea can explain the extremally high conductivity of the high explosives with the large fraction of free carbon.

We performed the molecular dynamic simulations of the condensation of the carbon atoms in the DP using a simple model of the DP. The possibility of formation of carbon nets in the DP was confirmed. The calculations of the conduction of these nets are in a good agreement with the measurements of the conductivity of the DP.

Molecular dynamics simulations

The main question we are going to clear up in this study is how much carbon is needed to form a conductive structure in the DP of solid explosives. So we do not need a highly detailed model of the DP including carbon atoms. Thus, we do not take into account fine features of chemical interactions. The simplest model which can answer the question includes two sorts of particles interacting in some simple way. The particles of the sort C represented the atoms of free carbon whereas the P-sort particles were the other detonation products. Thus, the molecular dynamics of the ensemble consisting of these two sorts of the particles (atoms) was studied. Pair interactions between particles of the same sort and between particles of different sorts were simulated with the Lennard-Jones potential

$$U(r) = 4\,\varepsilon\left(\left(\frac{b}{r}\right)^{12} - \left(\frac{b}{r}\right)^{6}\right).$$

All the "atoms" had the same mass of 20 atomic mass units that approximately corresponded to the average weight of DP molecule. The parameters of the Lennard-Jones potential for different pairs of atoms were $\varepsilon_{CC} = 3.2 \cdot 10^{-19}$, $\varepsilon_{PP} = 0.01 \cdot \varepsilon_{CC}$, and $\varepsilon_{CP} = 0.01 \cdot \varepsilon_{CC}$ J. The value of b characterizing the atom size was assumed to be equal to $2.7 \cdot 10^{-10}$ m.

The value of the parameter ε_{CC} was taken so that to obtain the reasonable agreement between parameters of the melting point for the MD-ensemble in the calculations and the experimental data for carbon. All other parameters that characterize mainly the DP were chosen so as to fit the calculated pressure, the temperature and the density to the reasonable parameters behind the detonation wave $\rho = 2.5$ g/cm3, $p = 20$ GPa, $T = 3000$ K.

MD-calculations were performed in the region of size 20 nm x 20 nm x 20 nm. The total number of particles was 512000. The simulations started from the initial state with the fixed temperature and pressure and the approximately homogeneous distribution of the atoms in the region. The simulations were carried out for the values of the volume fraction of the carbon atoms from 2 to 40 percent. The carbon atoms aggregated to the dense particles with sizes of the several atomic diameters in all the cases. At such conditions, small particles coalesce into a large particle of the size about 2–3 nm and lose their individuality. The large particles are also combined together but without loss of the individuality (Fig.1).We can consider the large particles of size of $d \sim 3$ nm and more to be mechanically strong. They are found in the DP retained after explosion.

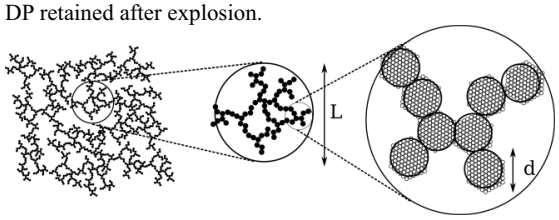

Fig.1. Multiscale model of carbon condensation, from particles to mesoscale nets.

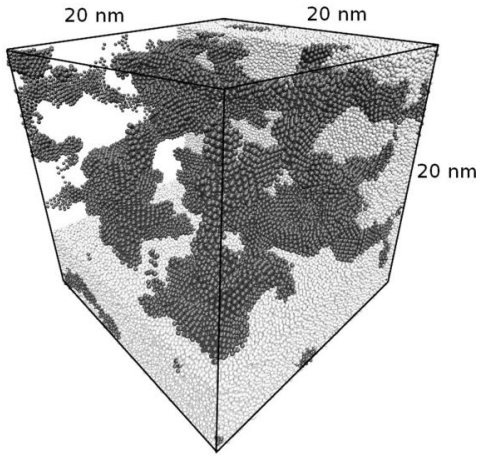

Fig. 2. Carbon condensation in the DP. The results of simulation. The light balls are the DP molecules. The dark balls are the carbon atoms, the volume fraction of the carbon atoms was 10 percent. Only the carbon component is shown in the part of the simulation region for clarity.

The carbon particles formed in the DP aggregate to sparse clusters with the large volume of pores between particles. Combining with their neighbors, the clusters grow in the sizes. The process is completed with one of two possible states depending on the cluster size. If the size of the cluster is large enough, the fluctuating forces of the DP bend and break the branches of the cluster that restricts its final size. In the other case, the clusters make contact and form the conducting net. The typical carbon net obtained in simulation is shown in Fig. 2. The DP in the nearest part of the Fig. 2 are not displayed in order to represent the structure of the carbon net clearly.

Fig. 3 shows a micrograph of the solid residue after the explosion of the mixture of 50 percent TNT with 50 percent RDX consisting mainly of carbon. The micrograph was obtained with the JEOL JEM 2012 training transmission electron microscope. One can see that carbon particles combined with the formation of a spatially complex structure. Thus, the results of the MD simulations are in a qualitative agreement with experimentally observed carbon structures.

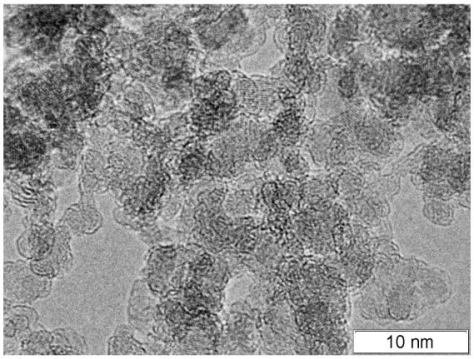

Fig. 3. Carbon condensation in the DP.

The conductivity of the carbon nets obtained in the MD simulations was also calculated.

Analysis of experimental data

The experimental data about the conductivity of the DP products of the explosive with various carbon content at the Chapman – Jouguet plane are required to understand the role of carbon in the DP conduction. We have analyzed the data on the conductivity of high explosives with various carbon content such as RDX, HMX, PETN [3, 4], compacted TNT of maximal density [5], bulk TNT and bulk TNT with water [6].

The content of free carbon in the DP was evaluated using the data of the calculation of the DP composition at the Chapman - Jouguet plane [7].

Fig. 4 shows the data on conductivity of a series of high explosives as well as their mixtures. The calculation of the free carbon fraction [7] shows that all these explosives release a significant quantity of free carbon to the moment when the state of the substance corresponds to the Chapman – Jouguet plane. The fraction of the free carbon atoms varied from 0.016 for bulk PETN (PETN, 1.1, Fig. 4) to 0.3 for the compacted TNT of maximal density (TNT, 1.6, Fig. 4). The data on the measured

conductivity of the DP are shown as the intervals in Fig. 4. The upper end of the each segment shows the maximal value of the conductivity within the von Neumann peak and the lower one corresponds to the conductivity value at the Chapman – Jouguet plane. We showed such a wide range of the conductivity values since the carbon net can arise, develop, and break in this region of the detonation wave. The number to the right of the data intervals represents the initial explosive density.

The free carbon fraction and the conductivity of the DP of a pure TNT measured in the experiments increase with the density. The maximal conductivity of 100 Ohm-1cm-1 was observed at the maximal density for compacted TNT (TNT, 1.6). The conductivity decreased dramatically with the decrease of the density. The smallest of the maximal values of the electric conductivity plotted at the Fig. 4 was observed at the density 0.95 g/cm3 and is equal to 25 Ohm-1cm-1 (TNT, 0.95). Hence, the magnitude of the conductivity decreases by the factor 40 with the density decrease by about 40 percent. This suggests to the existence of some non-ionic mechanisms of conduction. The data (TNT, 1.6 cast) corresponds to the cast TNT. The differences between the conductivity values for the cast and compacted TNT are explained usually by the some features of the detonation process.

The results for the mixture of TNT with the chemically inactive component (water) are shown in the Fig. 4 with designation tnt, 1.15 + H2O. The magnitude of the registered signal increases twice in comparison with the pure TNT of the bulk density. Since the water conductivity is about 0.1 Ohm-1cm-1 [8] at the pressures specific to detonation, this conductivity increase can not be explained with the increase of the quantity of the charge carriers supplied from water.

We concluded that water filled the volume free of explosive that resulted in the compactness of the DP. To represent these data with the point on the plot correctly, we recalculate the free carbon fraction. The experimental density of the TNT in its mixture with water was 1.15 g/cm3 and water filled the pores. The estimation of the volume fraction filled with the carbon atoms in the mixture of TNT with water was 0.08. The Tait equation for water was applied to calculate the water fraction in the DP. Then, the volume fraction filled with the DP of TNT is 0.82. The value of the conductivity of 23 Ohm-1cm-1 was measured at the experiment. We recalculated this value to the conductivity of a pure TNT excluding water and obtained 32 Ohm-1cm-1. At the fixed volume, the density of TNT was $\rho = 1.408$ g/cm3. The approximation of the data from [9] leads to the value of 4.8 of carbon atoms released in a free chemical form per molecule of TNT, that is the volume fraction of the free carbon was 4.8/21 = 0.23.

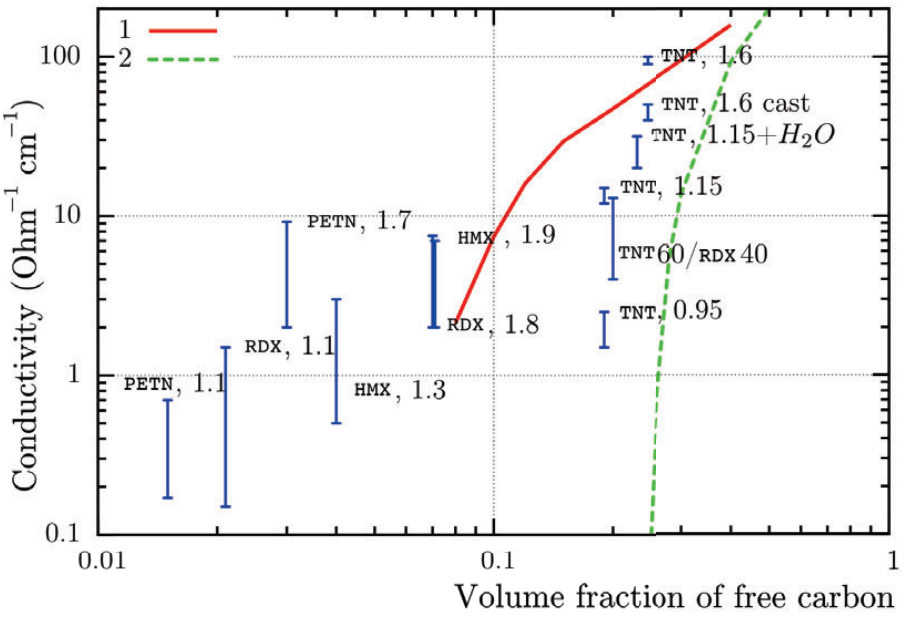

Fig.4. Electrical conductivity of detonation products. 1 – electrical conductivity of carbon nets simulated using MD, 2 – percolation model, points are the experimental data for different HE, the corresponding values of the density are shown near each point.

The data for the compacted mixture of TNT and RDX are marked with “TNT 60/RDX 40” in the Fig. 4. The DP of TNT are diluted with the more powerful RDX having lower conductivity. Thus, the DP of TNT were compressed with the DP of RDX that increased the pressure in the DP of TNT and changed the quantity of the chemically free carbon. In this case, the volume fraction of free carbon and the conductivity were recalculated with the method described above.

We should distinguish between two regions at the plot in the Fig. 4 that differ with the conduction mechanism. The first one includes the data for the explosives containing TNT and another one includes all other data.

The conductivity of the explosives with balanced chemical composition (the volume fraction of free carbon is lower than 8 percent) is significantly smaller than that with a large fraction of free carbon. The conductivity of the explosives with the carbon fraction less than 8 percent corresponds approximately to the conductivity of TNT with the carbon fraction about 20 percent. However, the thermodynamic parameters of TNT in the detonation wave are significantly lower than the parameters of that explosives and none of the other mechanisms (without using the conductivity of the carbon nets) can explain such high conduction of the TNT.

Results

Condensation of carbon atoms to clusters and spatial nets in the detonation products was simulated using molecular dynamics method. It was shown that the fraction of free carbon for about 8 percent is sufficicent in order to the carbon nets start to form. The electrical conductivity of the resulting carbon nets was calculated for different volume carbon concentrations. It is shown that the formation of the carbon nets is a mechanism that can really explain the high values of conductivity of the DP of the carbon-rich condensed explosives behind the detonation wave.

Acknowledgments

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