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The dynamics of carbon nanostructures at detonation of condensed high explosives

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Based on the obtained earlier experimental conductivity graphs at detonation of five different high explosives, an analysis was performed which shows a correlation between the carbon content and the conductivity magnitude. An assumption was put forward that the conductivity in the whole detonation wave is provided by the contact mechanism along conductive carbon nanostructures.

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INTRODUCTION

Detonation products (DP) of condensed high explosives (HEs) of the kind $C_aH_bN_cO_d$ contain carbon structures of different types: soot, diamond, and amorphous carbon. The ultrafine diamond (UFD) is of particular interest^{1,2} due to its application in industry. Presently, there are several questions which are still not clear. Thus, there is no common opinion about the time of nanodiamond formation, and the formation mechanism is not clear.³

The process of carbon condensation in a detonation wave leads to the UFD formation, and this process is in turn connected with the kinetics of chemical reactions. Experimental investigation of the kinetics is complicated due to intrinsic features of fast processes, namely, short duration (several microseconds) and aggressiveness of the investigated medium (high pressures of tens of GPa and high temperatures of several thousand degrees). Therefore, the kinetics is mainly studied by the numerical methods, and its features are recovered from the final results by investigating the structures extracted from DP after a chemical treatment.

Dynamics of the UFD formation can be traced by the electric conductivity, which is the result of the presence of carbon nanostructures as will be discussed later. Comparison of the literature data on the chemical peak duration and the time dependence of conductivity $\sigma(t)$ has earlier shown that if a pronounced conductivity peak is present, its duration is close to the duration of the zone of chemical reaction.^{4,5} This allows one to observe the kinetics related to the carbon almost directly based on the conductivity graph $\sigma(t)$.

Despite more than half-century research history, the nature of high conductivity at the detonation of condensed HEs is still uncertain. There is no generally acknowledged assumption of the predictive power. The investigation of conductivity is however highly promising. With the detailed understanding of the mechanism of conductivity, it could become a highly sensitive and simple tool to investigate the nanostructural changes of the medium with several advantages: only weak disturbance of the process investigated, the diagnostics directly in the high-pressure region, and in real time.

Several possible conductivity mechanisms were considered so far: thermal ionization,⁶ thermal ionization in dense matter,⁶ thermal emission,⁷ ionic mechanism,⁷ chemical ionization,^{8,9} contact mechanism,^{10–12} and ionization of water.¹³ However, none of them have become a hypothesis of the predictive power. At present, the most common hypothesis is that in HEs with negative oxygen balance, the conductivity in the chemical peak results from the chemical ionization, and the conductivity in the Taylor wave is ionic. Generally accepted point of view is that in the TNT, the electric properties are determined by the carbon, and there is certain connection between the carbon content in the Chapman–Jouguet point (CJP) and the conductivity for HEs with small carbon content. Whether this is the main factor was not investigated and not proved.

In 1965, Hayes proposed the correlation between the maximum value of the conductivity at the detonation and the free carbon content in the DP.¹⁰ He also proposed the contact mechanism of the conductivity along the carbon nanostructures which serve as “wires.” The density of condensed carbon was obtained numerically taking into account the compression of medium in the detonation wave. The density was taken in the CJP, and the maximum value of the conductivity was used although the question about the correlation between the conductivity and the detonation wave is still open.

The assumption of the present paper differs from the aforementioned ones in the following point: for the first time, the maximum value of conductivity for five HE is connected with the total carbon content, and the conductivity in the CJP is connected with the free condensed carbon.

The relation between the maximum conductivity and the total carbon content was only mentioned in the work of Gilev.^{11,12} There, based on the percolation model, the carbon content was claimed to be insufficient for the explanation of high conductivity in TNT ($\approx 250 \Omega^{-1} \text{cm}^{-1}$). The necessary existence of long highly conductive structures already in the chemical peak was pointed out. The explanation of the dynamics of conductivity, the determination of the influence of thermodynamic parameters, and the development of a model are actual now.

The correlation obtained from the experimental data allows us to claim that the conductivity in the whole

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detonation wave is provided by the carbon nets in conductive phase except the cases with low volume fraction of carbon (less than 0.07 (Ref. 14)). Thus, the dynamics of conductivity tracks the evolution of carbon nanostructures. The analysis of the experimental results obtained in the Lavrentyev Institute of Hydrodynamics SB RAS^{4,5,15–17} was carried out.

EXPERIMENTAL DATA AND DISCUSSION

The detonation wave consists of the shock front, the adjacent chemical peak (von Neumann peak) where chemical reactions occur, and the Taylor rarefaction wave separated from the chemical peak by the Chapman–Jouguet point where the velocity of products is equal to the local speed of sound. In the Zeldovich–von Neumann–Doering, theory, the chemical reactions are completed in the CJP.

The typical graph of conductivity at the detonation of condensed HE is shown in Fig. 1. The value of conductivity increases up to the maximum σ_{max} during several tens of nanoseconds, then it rapidly decreases to the point marked as σ_{CJ} , which corresponds to CJP, and the region of slowly varying conductivity in the Taylor wave. The figure shows the end of the chemical reaction zone defined by a crossing of straight lines.

At present, there is no theoretical foundation of the connection between the conductivity graph and the detonation wave; therefore, we discuss in detail their correlation in the framework of the assumption proposed. For the investigated HEs, the conductivity of the chemical peak σ_{max} is greater than σ_{CJ} .⁵ Therefore, the assumption was proposed that the maximum conductivity σ_{max} is provided by the total carbon content, whereas the conductivity in the CJP σ_{CJ} is due to the condensed carbon. Thus, the carbon structures grow until the upper point of the chemical peak, and the reactions with carbon occur later, in the range between the points marked as σ_{max} and σ_{CJ} in Fig. 1. In the CJ point, reactions are completed, the carbon nets are thinned and partially broken, and the conductivity $\sigma_{CJ} < \sigma_{max}$ is provided by the remaining structures. The following decrease of the conductivity is due to the partial disruption of conducting branches in the dense DP medium and the possible partial transition of the carbon to a non-conductive phase.³

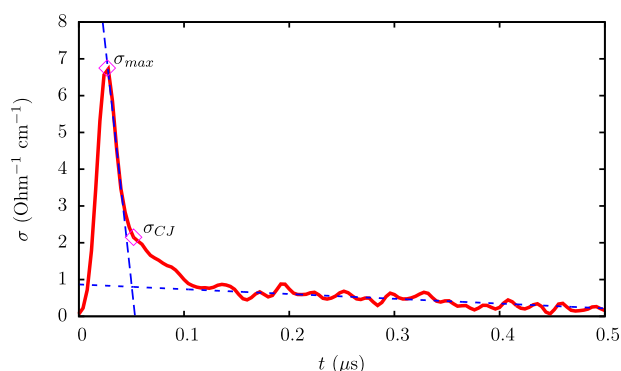


FIG. 1. Profile of electrical conductivity at detonation of HMX, σ_{max} —maximum conductivity, σ_{CJ} —electrical conductivity in CJP. The figure shows the end of the chemical reaction zone defined by a crossing of straight lines.

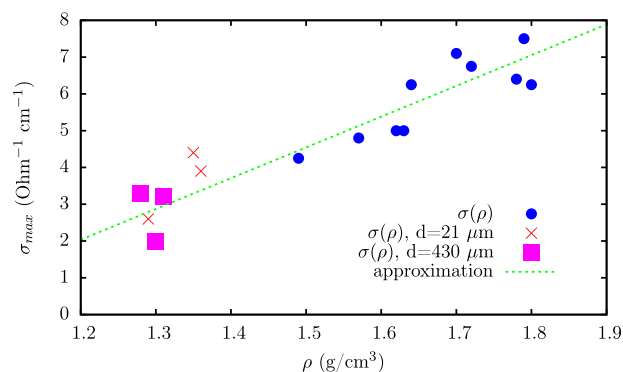


FIG. 2. The values of maximum conductivity at different initial density for HMX.

The lower is the initial HE density, the higher is the influence of the charge inhomogeneity. In order to connect correctly the relative fraction of carbon in the molecule with the conductivity, the value of σ_{max} is necessary, which is hard to obtain with the experimental technique used. Therefore, we constructed approximated based on the experimental data and made an extrapolation to the crystal density.

Figure 2 shows the values of σ_{max} for HMX at different initial density and the linear approximation. At powder densities $\rho < 1.4 \text{ g/cm}^3$ the large scatter is due to different grain size (21 and 430 μm (Ref. 17)), which affects both the conductivity value and the width of the reaction zone. The increase of σ_{max} is clearly seen. This trend is common for all the investigated HEs.

Based on the data of Ershov *et al.*⁵ where the conductivity for different densities was obtained, we constructed the approximation of σ_{max} for cyclotrimethylene-trinitramine (RDX), cyclotetramethylene-tetranitramine (HMX), pentaerythritol tetranitrate (PETN). Results are shown in Fig. 3. The maximum conductivity σ_{max} increases with the increase of density, which is connected with the increase of the density of carbon and carbon nanostructures.

Linear extrapolation of σ_{max} to the crystal density for trinitrotoluene (TNT) and triaminotrinitrobenzene (TATB) was made based on the powder density and the maximum obtained one.^{15,18,19} For TNT, the results of Hayes¹⁰ were also taken into account.

Based on the data of Tanaka,²⁰ the mass fraction of carbon in the CJ point r_{CJ} at different initial density was calculated by the interpolation. Figure 4 shows some data of

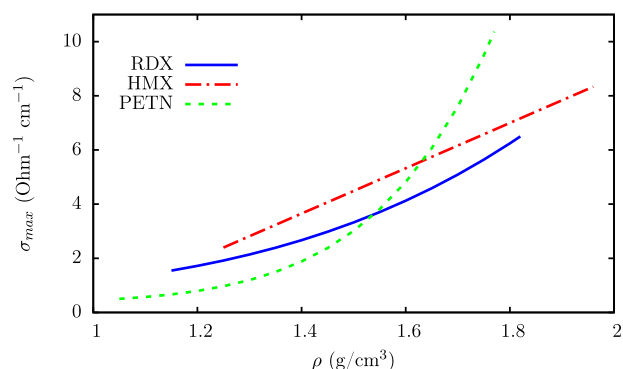


FIG. 3. The approximation of experimental data of σ_{max} for different HEs.

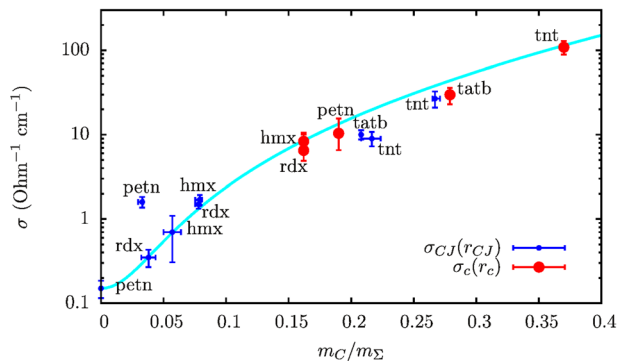


FIG. 4. $\sigma_c(r_c)$ —the values of maximum of conductivity at crystal density (the result of extrapolation), $\sigma_{CJ}(r_{CJ})$ —electrical conductivity in CJP.

Ershov^{4,5,15–18} on the dependence of σ_{CJ} on the mass fraction of the condensed carbon $\sigma_{CJ}(r_{CJ})$ and the values of maximum of conductivity at crystal density $\sigma_c(r_c)$ (extrapolation results).

There is a pronounced dependence of both the maximum conductivity σ_c and the conductivity in the CJ point σ_{CJ} on the carbon fraction. Graphs $\sigma_c(r_c)$ and $\sigma_{CJ}(r_{CJ})$ are close.

Taking into account the increase of the free carbon release with the increase of density, it follows from the experimental data that the value of $\sigma_{CJ}(r_{CJ})$ for intermediate densities lies in the interval between the values for maximum and minimum densities shown in the graph.

In the work of Prueel *et al.*,²¹ the molecular dynamics simulation of the formation of carbon structures in detonation products was carried out. Based on the structures obtained, the conductivity of the medium was calculated. It was assumed that the structures consisted of graphite with the conductivity of $\sigma_0 = 1000 \Omega^{-1} \text{cm}^{-1}$. In the detonation products of TNT, together with compact rounded particles, filamentary graphite structures a few nanometers thick and about 50 nm long were found.^{2,22} These structures are remnants of carbon nets formed at detonation.

At a certain carbon fraction, the formation of connected nets become impossible due to the lack of conductive substance. In the works of Prueel,^{14,21} the threshold carbon fraction of 0.07 was determined in numerical experiments, which theoretically allows the formation of connected nets in DP. Based on the data shown, it is possible to say, that carbon influences the conductivity also at fractions lower than 0.07. In such cases, different mechanism related to the carbon can exist, e.g., distribution of highly conductive nanostructures in a medium with low conductivity. For PETN, high value of the conductivity σ_{CJ} at the carbon fraction of $r_{CJ} = 0.033$ could be explained by peculiarities of chemical reactions, where the oxidation mainly leads to the thinning of structures rather than their breakup.

The model proposed is confirmed by the following works:

(1) In the work of Breusov²³ it was shown that the formation of UFD cannot be connected with the intermediate production of the free carbon, and the mechanism for the UFD formation was proposed which is connected with the partial breakup of molecular bonds and the formation of the growth of the carbon net.

- (2) In the works of Anisichkin^{24,25} claims based on the analysis of experiments with isotopic tag that the carbon oxidation occurs later than the formation of carbon particles, and confirms the fast nucleation of carbon atoms. This agrees well with the data shown.
- (3) HEs considered in this paper have different parameters of detonation;²⁰ the detonation diamonds were found in products of most of them. When the diamond forms in the chemical peak, this should be seen on the conductivity graph because diamond is a dielectric.²⁶ However, the dependence $\sigma_c(r_c)$ has no explicit traces of the diamond formation. Therefore, we can suppose that carbon exists in the region of the chemical peak in a conductive phase for all the HEs investigated. In the phase diagram of carbon²⁷ the state of CJP of studied explosives was into the condensed phase. In work of Danilenko,³ it was obtained for TNT, RDX, TNT/RDX mixture, and TATB that the conditions in the CJ point are shifted to the region of liquid nanocarbon when the size of nanodiamond is taken into account. The author claims that diamond is formed from the liquid phase in the rarefaction wave. In the work,²⁸ the conductivity of liquid carbon was measured experimentally at the temperatures characteristic for the detonation. Its value of $\sigma \approx 10^3 \Omega^{-1} \text{cm}^{-1}$ explains the high values of conductivity σ_c and σ_{CJ} obtained in experiments. Such value can be reached at the contact conduction along the carbon structures connecting the interelectrode gap. The conductivity of highly-oriented graphite can reach the value of $2 \cdot 10^4 \Omega^{-1} \text{cm}^{-1}$.²⁸ Both graphite and liquid carbon have the high conductivity $\sigma \approx 10^3 \Omega^{-1} \text{cm}^{-1}$ ²⁹ therefore, the existence of both graphite and liquid conductive carbon nanostructures is possible.
- (4) In the works,³⁰ the data on the small-angle x-ray scattering (SAXS) at the detonation were obtained using synchrotron radiation. Since the scattering occurs on inhomogeneities, the magnitude of SAXS is proportional to the density difference squared of the medium and the inhomogeneity. The increase of the integral SAXS intensity is smooth without jumps in the chemical peak region which should be present if the UFD formation is completed in the von Neumann peak. The density of the liquid carbon phase at the temperatures of 5000–7000 K and the pressure of 0.1 kbar is $\approx 1.8 \text{ g/cm}^3$.²⁹ Therefore, if the carbon structures are liquid, the contrast is low, and the structures are not resolved due to small density difference of DP and carbon inhomogeneities. The smooth growth can be interpreted as the observation of the phase transition dynamics which result is the UFD. All the facts mentioned support the model proposed.

We investigated the influence of different chemical elements on the maximum conductivity σ_{max} and the conductivity in the CJ point σ_{CJ} . Only the correlation with carbon was obtained.

Analysis of the data on mixed HEs is more complicated, although the overall trend of the conductivity increases with the carbon fraction. The grain size plays a significant role of the HEs mixed. Different HEs were investigated. Influence of the grain size in TNT/RDX mixtures was thoroughly

studied in the work.¹⁶ The maximum conductivity decreased with the decrease of the grain size. Emulsion HEs were investigated in the work,^{31,32} the mixture of TNT with ammonium nitrate was investigated by us. The mixture of TNT with ammonium nitrate has zero oxygen balance at certain composition, and it produced at a powder density the extremely low conductivity about $0.01 \Omega^{-1} \text{cm}^{-1}$. This result agrees well with the assumption of the key role of carbon.

The problem of conductivity is multiparametric. There is a correlation with the pressure for HMX, RDX, and PETN mentioned in the work.⁵ The density and the temperature also affect the conductivity.

For determining the role of carbon, the authors of landmark papers^{10–12} considered the influence of the density of carbon. In the detonation wave, the density changes gradually. In the chemical peak, the matter can be compressed to the density two times larger than the initial one. In addition, the degree of compression can be different for different substances. Thus, carbon can be compressed less than nitrogen. Therefore, the density of carbon is unknown and not reliable. In contrast, there is no such uncertainty for the mass fraction of carbon; it remains the same even under compression. In the coordinates “mass fraction of carbon–electric conductivity,” the influence of other factors is minimized. This allows to extract the decisive role of carbon. Interestingly, in these coordinates, the relations for the maximum value and for the value in the CJP become universal.

CONCLUSION

We performed an analysis of the experimental data on condensed HEs in a wide range of the carbon mass fraction from 0 to 0.37 and the electric conductivity from 0.15 to $109 \Omega^{-1} \text{cm}^{-1}$. Boundary values correspond to the CJP of the powder density PETN and the crystal density TNT, respectively.

We obtained a correlation between the carbon content and the conductivity in the whole detonation wave. High values of the conductivity are explained by the contact mechanism which is provided by conductive carbon connected nanostructures.

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