



Rate of the Energy Release in High Explosives Containing Nano-size Boron Particles

Gennady I. KANEL*, Alexander V. UTKIN
and Sergey V. RAZORENOV

*Institute of Problems of Chemical Physics RAS
Chernogolovka, Moscow reg., 142432 Russia*

**E-mail: kanel@ficp.ac.ru*

Abstract: With a goal to obtain information on rate of the high explosive decomposition and equation of state of the HE formulations and detonation products, measurements of the pressure and particle velocity profiles of shock and detonation waves have been performed for pure coarse-grain and fine-grain HMX and for the HMX+16.4% boron mixture. For these measurements, the manganin pressure gauges and the laser Doppler velocimeter VISAR were applied. Effect of boron in the energy release process was observed both in the detonation and shock-wave initiation regimes.

Keywords: high explosive, HMX, boron, manganin pressure gauges, VISAR, Chapman-Jouget point

Introduction

Metal powders, mainly aluminum, have commonly been incorporated as additives in composite high explosives (HE) to enhance the performance of the energetic mixtures. Formation of the metal oxides increases the temperature of detonation products, alters the equilibrium product distribution, and directly influences the rate of energy delivery from the explosive. Despite the wide usage of metal-filled composite explosives, the chemical kinetics and reaction mechanisms of the metal oxidation at detonation pressures and temperatures have not been detailed.

Metals have been used as an additive enhancing detonation characteristic

of high explosives since the beginning of last century [1, 2] and find extensive application both in industrial and military explosives. It has been revealed that compositions of high explosives with aluminum, boron, or beryllium, as a rule, have an increased explosion heat and strength in demolition effect. The brisant effect remains nearly invariable with introduction of metal up to 20% into the high explosives. The influence of metals on the detonation velocity and pressure can be different as a function of metal concentration and particle size, but at least for HE with negative oxygen balance these properties go down. The positive effect is provided by oxidation of metals at reduction of CO₂ and H₂O content in the detonation products. Reactions of metals with carbon and nitrogen are not profitable and give a negative effect.

Several experimental investigations of the wave profiles at detonation of the HE+metal mixtures have been performed [3-8]. The results indicate that the additive of Al significantly complicates the structure of detonation waves, which depends on different characteristic times of HE decomposition and Al oxidation. The problem is that Al can oxidize both in the reaction zone and behind of the Chapman-Jouget (CJ) plane.

A comprehensive review on detonation properties of HE mixtures with aluminum has been published by Aniskin [9]. The conclusion has been drawn that in the reaction zone of power high explosives the aluminum particles of $>1\ \mu\text{m}$ size do not react with the detonation products and their influence on the detonation parameters is analogous to that of inert additives. The energy release associated with oxidizing aluminum particles of $\sim 5\ \mu\text{m}$ size becomes essential in $\sim 4\ \mu\text{sec}$ behind the detonation front and is continuing for at least 20-30 μsec . The effect of aluminum on later stages of the detonation process was confirmed by recording the expansion rate for metal tubes filled with the HE and by measurements of the launching velocities for metal plates. The enhanced detonation parameters were recorded only for mixtures of aluminum with strong oxidizers at a micron size of the components grains. These oxidizers individually are not power explosives and are characterized by a relatively large (2-4 μs) duration of the reaction zone in detonation wave.

Much less investigations were conducted on mixtures of high explosives with other metals. Unlike aluminum, the products of the boron oxidizing, B₂O₃, HBO₂, B₂O₂, and BO, are gases. Due to that, one may hope for considerable increments in the detonation velocity and pressure for the HE formulations with boron. In ref. [10] the explosion heat and chemical composition of detonation products of PETN+B and RDX+B mixtures were studied. The explosion heat increases with adding 16.5 wt.% B up to 1880 kcal/kg and after that decreases with the following growth of amount of boron in the mixture. In the case of

PETN, the explosion heat reached 2050 kcal/kg at 22 wt.% of boron while for the pure PETN this value was 1400 kcal/kg. However, the detonation products besides the carbon and boron oxides contain the boron nitride BN and the boron carbide B₄C which are in a condensed phase and should decrease the detonation parameters. Results of measurements of the detonation velocity for PETN+B mixtures have been published in ref. [11]. Experiments were done with HE of ~5 μ grain size and the boron particles of 0.1 μm diameter. It has been shown that the detonation velocity decrease for the PETN + 11 wt.% B mixture amounts ~3% as compared to the pure PETN of the same densities (0.83 to 1.73 g/cm³). At high density an essential growth in the detonation velocity was observed with increasing the charge diameter up to 3 cm. An obvious improvement in the detonation velocity and failure diameter of the explosive compositions based on NH₄NO₃ was observed by Sosnova [12] when 10-15% of boron or aluminum was added. Such explosive compositions are actually mixtures of a fuel and strong oxidizer. The effect was much larger when 5% of PETN was added to the mixture, however in general the detonation velocity and pressure still remained lower than that of powerful individual high explosives.

Explosive materials tested

HMX and HMX+B mixtures have been chosen as the objects for investigations. Since the HMX molecules contain the same elements and in the same proportion as RDX, we have concluded that 16.5 wt.% of the boron content should provide a maximum explosion heat for the HMX+B mixture like the RDX+B composition [10].

Three series of similar experiments have been carried out for pure coarse-grain HMX in the as-received state, for the fine-grain pure HMX, and for the mixture of fine-grain HMX with boron. The as-received HMX powder contained 2.5 wt.% of particles with a size of 400 μm, 83 wt.% of particles 160 to 400 μm, 14 wt.% of 63 to 160 μm particles, and 0.5% of particles with the size less than 63 μm.

The fine-grain HMX has been prepared using the following technology. The incidental HMX powder was solved in dimethylsulfoxide in the 30% concentration. Next, the solution was poured to water with a rate of 60 ml/min at agitating the mixture. The ratio of the HMX solution to water was 1:20, so the HMX/water ratio was 1:70. After precipitating the HMX, the mixture was filtered, the obtained HMX was washed three times with a big amount of water, and after that the HMX powder was again filtered and dried. The final moisture

content in the powder did not exceed 0.25 wt.%. Examination of the obtained powder has shown that the HMX particles have a size varying between 1 and 5 μm and the average density of grains is $1.858 \pm 0.003 \text{ g/cm}^3$.

For the composed HE, the amorphous boron powder B99A with the particle size in a range from 0.1 to 1 μm was used. The powder contained B: 99.5 wt.%, Cl: 0.02 wt.%, Fe, Mg, Pb, Al, Cu not more than 0.5 wt.% in total. After the drying the moisture content did not exceed 0.36 wt.%. The boron particles density was $2.181 \pm 0.003 \text{ g/cm}^3$.

83.6 wt.% HMX and 16.4 wt.% B were mixed in a rotated stainless steel barrel using the Teflon balls at the rotation speed of 60 revolutions per minute. For the mixing, some amount of hexane was added. Afterwards, the hexane was removed by drying and was not revealed in the final powder mixture.

The high-density samples for testing, 80 to 120 mm in diameter and 10 to 40 mm high were compacted by pressing. Since the press machine used can provide up to 100 t of the pressing force, the density of all samples of the same explosive material was adjusted to the maximum available density of samples of the largest diameter. The three formulations tested had different compacting abilities, so finally we tested a coarse-grain as-received HMX of 1.73 to 1.77 g/cm^3 density, the reprecipitated HMX of $1.66 \pm 0.01 \text{ g/cm}^3$ density, and the HMX+B mixture of $1.56 \pm 0.01 \text{ g/cm}^3$ density.

Experimental techniques

The experimental researches included measurements of the detonation parameters: detonation wave velocity, pressure and particle velocity profiles, reaction time. All experiments were performed in an explosive chamber without evacuation. Shock waves in the tested samples were created using explosive facilities. The pressure histories were recorded on the interface between the base plate and the sample with manganin pressure gauges [13]. The steady detonation wave structure was recorded with the VISAR laser velocimeter [14] that has provided a nanosecond time resolution of the measurements. These data provided the detonation pressure value and the chemical peak duration, that is of the range of practical interest for the HE decomposition time at the highest pressure.

A direct way to study the macrokinetics of HE decomposition in shock waves is based on recording the series of pressure or particle velocity histories in many points on the way of a shock wave in the HE sample when shock-to-detonation transition occurs and the following Lagrangian analysis of the data is performed [15]. However, such approach requires a large number of the experiments at a very

high accuracy of the measurements. Furthermore, it is known that any gauges placed inside the HE sample for the measurements disturb the investigated process. In determining the macrokinetic relationship using an approach based on comparison between the results of measurements and computer simulations of the experimental situations, there is no need to record the overall evolution of the initiating shock wave. Simpler tests can be used for this purpose, such as recording of the wave profiles at the interface between the HE sample being tested and an inert base plate through which a shock wave is introduced into the explosive sample. At high pressure, measurements of the reaction zone of a steady detonation wave are recorded to evaluate the decomposition time and for comparison with simulated wave profiles. Figures 1 and 2 show schemes of these experiments.

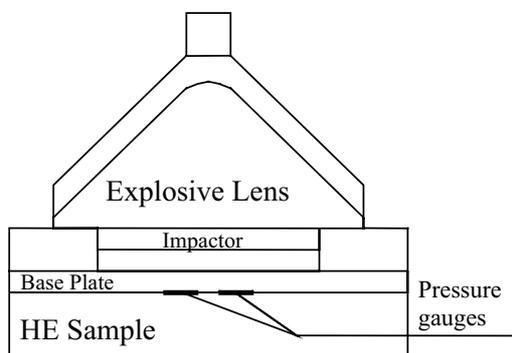


Figure 1. Scheme of experiments with recording the pressure history at the shock to detonation transition.

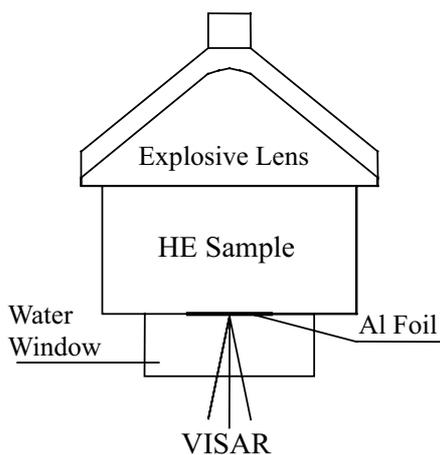


Figure 2. Scheme of measurements of the reaction zone of detonation wave.

The initiating shock wave was created in the HE samples by impact. In the most of such experiments aluminum plate impactors of 7 mm in thickness and 90 mm in diameter were launched with velocity of 1.17 ± 0.03 km/s using explosive lenses of 100 mm diameter. The sample was placed on a base plate. The pressure histories were recorded with manganin pressure gauges placed between the sample and the base plate. The gauges of ~ 6 Ohm resistance were insulated by Teflon films with 0.15 mm of a total insulation thickness. Two manganin gauges were used in each shot. To vary the initial shock pressure, the experiments were conducted with base plates made of aluminum, copper, and PMMA which have different dynamic impedances.

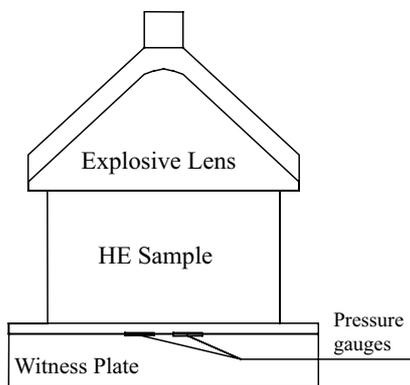


Figure 3. Measurement of the pressure history in detonation wave.

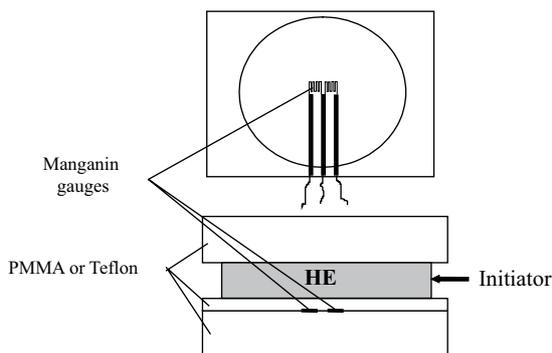


Figure 4. Scheme of recording the pressure histories in the transversal direction.

The chemical reaction zone of steady detonation wave was measured with the VISAR velocimeter using a water window and an aluminum foil reflector

on the sample-window interface. An advantage of the water window is a very good contact on the interface. The good contact between the sample and the foil was provided at the HE compacting procedure. Because of the impedance mismatch between the foil reflector and the HE sample, to provide a high time resolution of the measurements the foil should be either much less than the reaction zone length or a little exceed it. Since we expected very short reaction zone, for thin reflector we should use a foil of micron thickness. However, the residual porosity of the HE samples and a high detonation temperature do not permit to use thin foils if their thickness is comparable with the HE grain size. The measurements have been performed with the reflector thickness varied from 100 μm to 800 μm .

To monitor the detonation wave structure for a larger time, the pressure history was recorded in a thick Teflon witness plate placed behind the explosive charge (Figure 3). The HE samples in these experiments were 80 mm in diameter and about 40 mm in thickness.

Figure 4 presents the experimental configuration for recording the pressure history generated in witness plates by oblique detonation waves. A goal of these experiments was to get information for later stages of the detonation process. Since the manganin gauges used had dimensions of $\sim 7 \times 6$ mm, the time resolution of these measurements was not very good but the results can be used for comparison of the responses of different formulations.

The detonation wave speed was measured by a standard method using the ionization sensors.

Results of experiments

Detonation wave speed

Figure 5 presents results of measurements of the detonation wave speed in the HMX+16.4% B mixtures as a function of the initial density. In the Figure 5 the data are compared with detonation parameters of pure HMX and RDX [16, 17]. Since the HMX molecules contain the same elements and in the same proportion as RDX, these two explosives have the same heat of explosion, their detonation products are described by the same equation of state, and they have the same detonation wave speed as a function of the initial HE density. The relationship between the detonation wave speeds for pure HMX and HMX+B composition is similar to that for the HE mixtures with fine-disperse aluminum. Unlike the expected, the detonation wave speed is lower in the more energetic HMX+B composition.

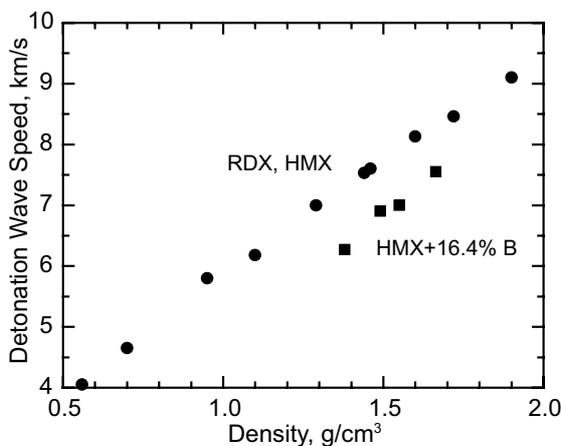


Figure 5. Detonation wave speed in the HMX+16.4% B composition as a function of the HE density in comparison with data for pure HMX and RDX.

Initiation

Figures 6-8 present the pressure profiles measured on the interface between the metal or PMMA base plate and the HE sample as it is shown in Figure 1. The measured pressure profiles on the surface of explosive samples are similar to each other and contain the following typical features. The first short pressure pulse of $\sim 0.1 \mu\text{s}$ duration corresponds to the initial shock pressure in the Teflon insulating films. After reflection of the shock wave from the HE sample surface the pressure corresponding to the impedance mismatch between the sample and the base plate material is established. The shock wave initiates the HE decomposition which results in the energy release, formation of the gas-like explosive products, and the pressure growth. Due to that the shock-to-detonation transition occurs.

Figures 9a, 9b illustrate main peculiarities of the pressure profiles. After the steady detonation sets in and the decomposition process near the sample surface is completed, the pressure and particle velocity on the interface come to values corresponding (the pressure-velocity diagram in Figure 9b), to the intersection point of the base plate deceleration Hugoniot and the release isentrope of detonation products from the Chapman-Jouget point. Therefore, measurements of the front pressure determine a point on the incident HE Hugoniot, while the final pressure is controlled by the release isentrope of the detonation products. Obviously, the pressure profile shape is determined both by the HE decomposition kinetics and boundary conditions on the interface. It is clear, for example, that initial slope behind the shock discontinuity is determined by the initial

decomposition rate; the slope should be zero if there is a notable induction period. The coming of signal to plateau is the upper estimation of the decomposition time in this pressure range. Thus, the measured pressure histories contain information both on the equation of state and the decomposition kinetics.

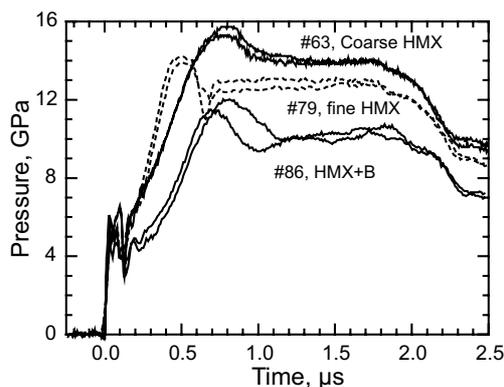


Figure 6. Pressure histories on the interface between HE samples and aluminum base plate (Figure 1).

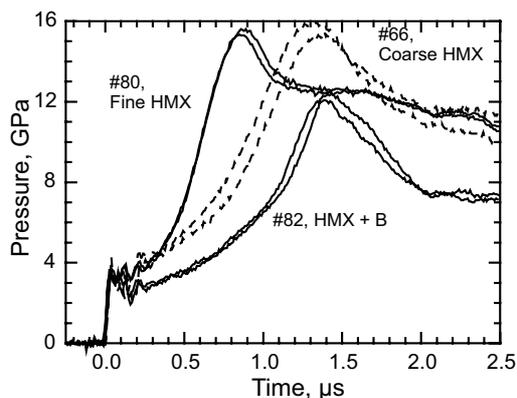


Figure 7. Pressure histories on the interface between HE samples and copper base plate (Figure 1).

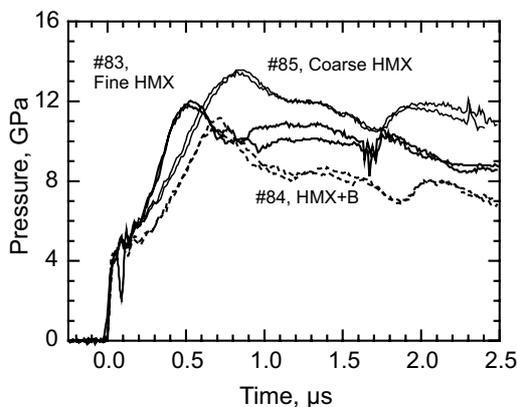


Figure 8. Pressure histories on the interface between HE samples and PMMA base plate (Figure 1).

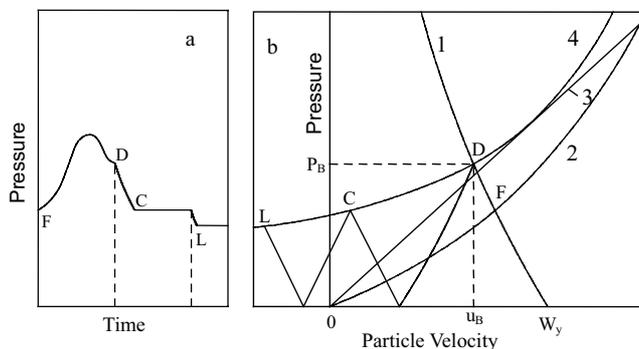


Figure 9. **a.** A typical pressure history at the interface between the HE sample and plane impactor or base plate; **b.** The pressure-particle velocity diagram where 1 is the deceleration Hugoniot for impactor or base plate, 2 is the incident HE Hugoniot, 3 is the wave beam $p=\rho_0 Du$ for the steady detonation wave with velocity D , 4 is isentrope of the detonation products passing through the Chapman-Jouget point. The point F corresponds to HE Hugoniot, points D, C, L correspond to the detonation products release isentrope.

The experimental profiles presented in Figures 6-8 are similar and indicate some finite energy release rate in the initial stage of the process and its acceleration in the following. All profiles display the pressure maximum which is more pronounced in experiments with base plates of higher dynamic impedance. The decomposition proceeds faster for fine-grain HMX than for coarse-grain

formulation. The final state is reached later for the HMX+B mixture than for pure HMX of both grain sizes, however, this does not mean yet the slower decomposition rate because the shock pressure is lower in the more porous mixture. We can also mention that while the initial portions of pressure profiles recorded by two gauges in one shot, as a rule, are well reproduced, the pressure maximum and the times of reaching the maximum often do not coincide. It seems that small variations in the initial conditions result in much greater variations of the shock-to-detonation transition time. Some difference in response of pure HMX and the HMX+B mixture is observed only after the pressure maximum. In the case of pure HMX almost constant pressure is maintained till the moment when the release wave comes from the impactor rear surface. In the case of the HMX+B mixture there is some certain increase recorded instead of the plateau in this part of the pressure history. Perhaps, this pressure growth is an evidence of energy release as a result of slower secondary process of the boron oxidizing.

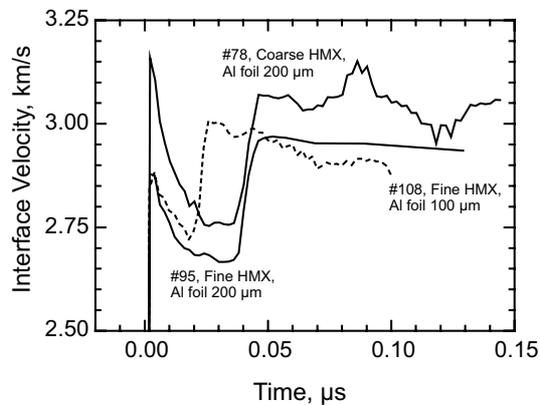


Figure 10. VISAR velocity profiles for steady detonation waves in pure HMX. Measurements with Al foil reflector and water window (Figure 2).

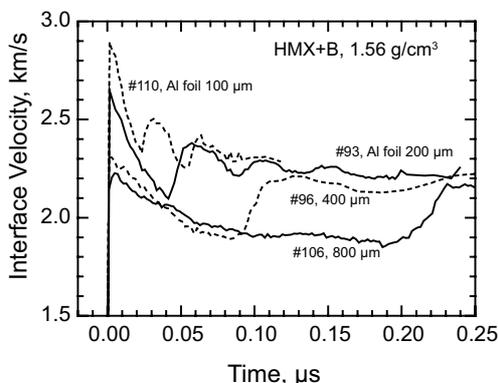


Figure 11. VISAR velocity profiles for steady detonation waves in the HMX+16.4% B mixture. Measurements with Al foil reflector and water window (Figure 2).

The chemical reaction zone

The particle velocity profiles for chemical reaction zone were recorded in the experimental arrangement shown in Figure 2 with the reflector foil thickness of 100 to 800 μm . The results shown in Figures 10 and 11 demonstrate that the chemical spike duration is quite measurable value by this technique. The second velocity increases and the following velocity oscillations are the result of wave reverberation within the reflector foil between the water window and the explosive. The decomposition process, again, is faster in the fine-grain HMX than in the coarse-grain formulation and is slower in the HMX+B mixture than in pure HMX. It is hard to define the time moment of the end of reaction zone but we certainly may conclude that the reaction time does not exceed 50 ns in the experiments with pure HMX and is about 100 ns for the HMX+B mixture. In the shot #106 with a thickest reflector foil the particle velocity profile for HMX+B mixture contains a plateau between ~ 0.1 and $0.2 \mu\text{s}$ which may be associated with undecompressed detonation regime as it was treated for the HMX+wax [6, 7].

Long-time observations of the pressure profiles

Figures 12-16 present the pressure profiles generated by the normal and oblique detonation of pure HMX and HMX+B mixture in thick PMMA and Teflon witness plates. In the case of PMMA the pressure profiles were distorted by the shock polarization signal. These experiments have been recognized as unsuccessful and were not used in the following analysis.

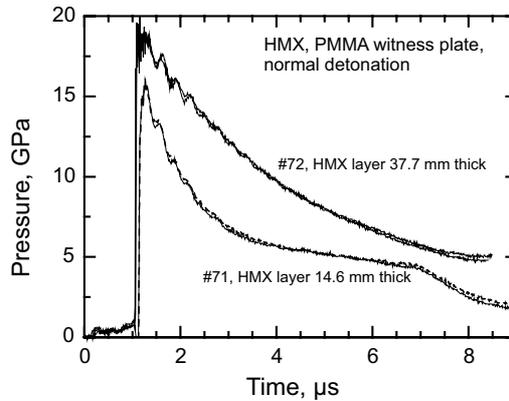


Figure 12. Pressure profiles generated by normal detonation of HMX in the PMMA witness plates. Measurements with manganin gauges (Figure 3).

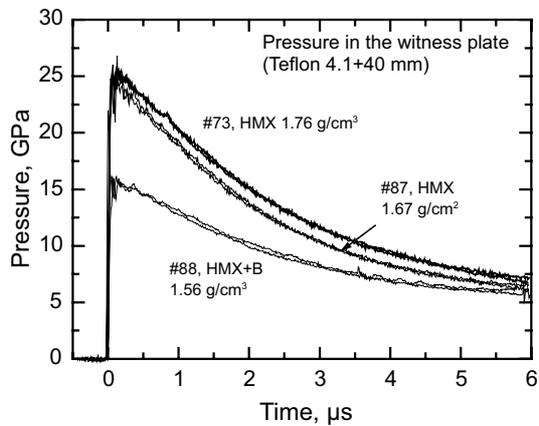


Figure 13. Pressure profiles generated by normal detonation of the pure HMX and the HMX+16.4% B mixture in the Teflon witness plates. Measurements with manganin gauges (Figure 3).

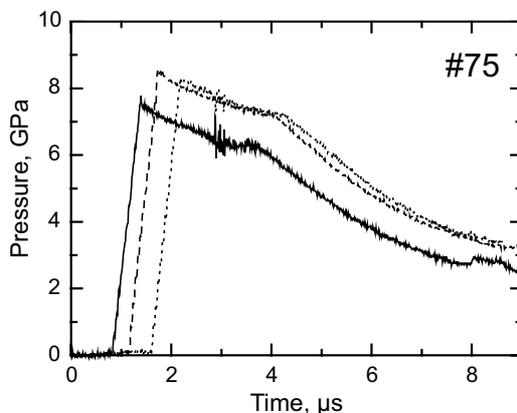


Figure 14. Pressure profiles generated by the oblique detonation of HMX in the PMMA witness plates. Measurements with manganin gauges (Figure 4).

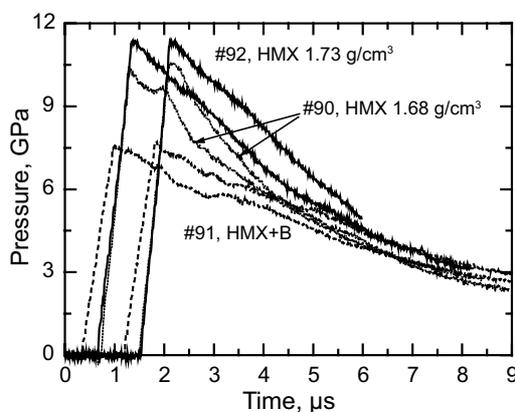


Figure 15. Pressure profiles generated by the oblique detonation of pure HMX and HMX+16.4% B mixture in the Teflon witness plates. Measurements with manganin gauges (Figure 4).

The results of measurements of pressure histories in thick Teflon witness plates loaded by the normal detonation wave do not demonstrate any qualitative difference in response of pure HMX and the HMX+B mixture. The peak pressure is much less for the mixture. However, comparison of the experiments with oblique detonation (Figure 16) shows a slower pressure decrease in the unloading phase for the mixture than for pure HMX, so in a later stage the residual pressure generated by the mixture exceeds the pressure generated by the pure HMX.

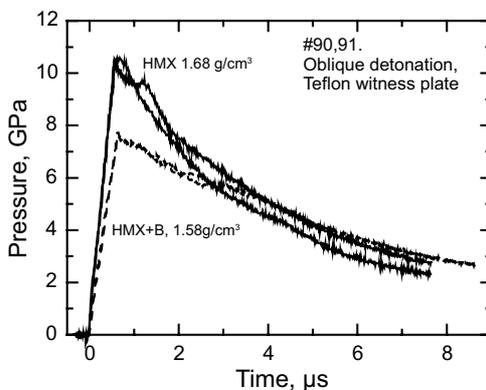


Figure 16. Comparison on one time scale of the pressure profiles generated by the oblique detonation of pure HMX and HMX+16.4% B mixture in the Teflon witness plates.

Discussion and conclusion

The effect of boron in the energy release process was observed both in the detonation and shock-wave initiation regimes. The positive effect appears in higher pressures generated by the oblique detonation waves at a later time (Figure 16). The residual pressure growth observed in the shock-wave experiments is shown in Figure 6. However, the boron gives a negative effect on the detonation parameters. It seems that the initial decomposition rate and the detonation parameters in the mixture are controlled by a heat exchange rather than by a chemical interaction between the HE decomposition products and the boron particles. The additional energy of the boron burning in the detonation products is released at a later time from ~ 0.1 - $0.2 \mu\text{s}$ to 1 - $2 \mu\text{s}$.

References

- [1] Belyaev A.F., *Combustion, Detonation and Work of Explosion of Condensed Systems*, Nauka, Moscow **1968**, (in Rus.).
- [2] Cook M.A., *The Science of Industrial Explosives*, IRECO Chemicals, Salt Lake City, Utah **1974**.
- [3] Aniskin A.I., Effect of Aluminium on the Profile of a Detonation in RDX Strongly Diluted with Inert Additives., in: *Detonation. Proceedings of the II All-Union meeting on detonation*, Chernogolovka **1981**, pp. 39-45, (in Rus.).

- [4] Moulard H., Fouguignon C., Lichtenberger M., Lombard J.M., Detonation de Melange Nitromethene-Al-NO₂, *Proceedings of the HDP Symposium*, CEA, France, Paris **1979**, pp. 293-307.
- [5] Tao W.C., Tarver C.M., Breithaupt D.R., Fundamental Chemical Interactions in Metal-Filled Composite Explosives, in: *Shock Compression of Condensed Matter 1991*, (S.C. Schmidt et al. Eds.), Elsevier Publishers B.V., **1992**, pp. 655-658.
- [6] Al'tshuler L.V., Balalaev V.V., Doronin G.S., Zhuchenko V.S., Obukhov A.C., Features of Detonation of Retarded HE, in: *Proceedings of II Soviet Workshop on Detonation*, published by the Institute of Chemical Physics, Chernogolovka, **1981**, pp. 36-39, (in Rus.).
- [7] Al'tshuler L.V., Ashaev V.K., Balalaev V.V., Doronin G.S., Zhuchenko V.S., Parameters and Detonation Modes of Condensed HE, *Physics of Combustion and Explosion*, **1983**, 19(4), 153-159.
- [8] Lubyatinsky S.N., Loboiko B.G., Reaction Zone Measurements in Detonating Aluminized Explosives, in: *Shock Compression of Condensed Matter 1995*, (S.C. Schmidt and W.C. Tao Eds.), AIP Conference Proceedings 370, **1996**, pp. 779-782.
- [9] Aniskin A.I., Detonation of Mixtures of High Explosives with Aluminum, in: *Detonation and Shock Waves, Proceedings of VIII Soviet Symposium on Combustion and Explosion*, published by the Institute of Chemical Physics, Chernogolovka **1986**, pp. 26-32.
- [10] Pepekin V.I., Makhov M.N., Apin A.Ya., Reactions of Boron at Explosion, *Physics of Combustions and Explosions*, **1972**, 8(1), 135-138.
- [11] Akimova L.N., Apin A.Ya., Stesik L.N., Detonation of HE with Boron and Its Organic Compositions *Physics of Combustions and Explosions*, **1972**, 8(4), 475-479.
- [12] Sosnova G.S., On the Burn of Boron and Aluminum at a High Pressure and Temperature, in: *Proceedings of III Soviet Symposium on Combustion and Explosion*, Nauka, Moscow **1972**, pp. 455-458 (in Rus).
- [13] Doherty R.M., Forbes J.W., Lawrence G.W., Deiter J.S., Baker N., Ashwell K.D., Suthertand G.T. Detonation Velocity of Melt-Cast ADN and ADN/Nanodiamond Mixtures, *Bull. American Phys. Soc.*, **1997**, 42(5), p. 1511, H1 4.
- [14] Bushman A.V., Kanel G.I., Ni A.L., Fortov V.E., *Intense Dynamic Loading of Condensed Matter*, Taylor & Francis **1993**, pp. 287.
- [15] Kanel G.I., Utkin A.V., Fortov V.E., The Equations of State and Macrokinetics of Decomposition of Solid Explosives in Shock and Detonation Waves, in: *Soviet Technology Reviews/Section B: Thermal Physics Reviews*, (Scheindlin A.E. and Fortov V.E., Eds.), Harwood Academic Publishers GmbH, **1992**, vol. 3, part 3, pp. 1-86.
- [16] Dremine A.N., Savrov S.D., Trofimov V.S., Shvedov K.K., *Detonation Waves in Condensed Media*, Nauka, Moscow **1970**, (in Rus.).
- [17] Finger M., Lee E., Helm F.H., Hayes B., Horning H., McGuire R., Kahara M., Guidry M., The Effect of Elemental Composition on the Detonation Behavior of Explosives, *Sixth Symp. (Int.) on Detonation*, ACR-221 of Naval Research, **1976**, pp. 710-722.