Effect of boron on HEM radiant ignition characteristics

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Abstract. The paper presents the ignition characteristics of high-energy materials (HEMs) containing ammonium perchlorate, butadiene rubber, and a mixture of Al/B nanopowders with different component ratios. Bimetallic systems based on aluminum with boron increase the reactivity and intensify the ignition of boron particles, which helps to decrease the critical ignition conditions of HEMs during heating. It is shown that the use of systems based on aluminum-boron reduces the delay time (by 17–52 %) and the ignition temperature of propellants in comparison with a HEM containing aluminum powder, and increases the activation energy of HEM during radiant heating.

1. Introduction

The energy-intensive fuels in the form of powder systems significantly improve the characteristics of steady ignition and combustion of composite solid propellant compositions [1–3]. Due to the high combustion value, boron-containing compositions may be considered as modern combustible components in the design of hybrid propellants and high-energy materials (HEM). The melted oxide layer of B_2O_3 is formed during combustion at relatively low temperatures, which prevents diffusion of the oxygen and its complete oxidation. The research findings have shown that the mechanical mixtures of various metals with boron reduce the accumulation of a liquid oxide layer on the particles surface and intensifies their combustion [2, 4–7].

The research findings on the study of bimetallic powder system characteristics note that Me-B mixtures are characterized by short ignition times [7] and lower ignition temperatures [8] in comparison with metal boride. The ignition time of boron/aluminum particles' mixture is shorter than for AlB_2 particles. Although the self-sustaining combustion time and the combustion intensity of B/Al mixture are lower [7]. Bulanin et al. [8] note that the ignition temperature of boron-aluminum air suspension is 50–150°C lower than the ignition temperature of AlB_2 particles. In their study [9] dedicated to oxidation, ignition and combustion behaviors of boron-magnesium composites, authors indicate that the ignition temperature of the composition based on B/MgB_2 and the required heat flux have lower values than for a mixture of B/Mg or boron. In addition, the B-Mg mixture combustion is faster than that of boron or B/MgB_2 composition in air-acetylene flame due to the rapid oxidation of elemental Mg in carbon dioxide.

This paper presents the experimental data of the ignition characteristics of HEMs containing ammonium perchlorate (AP), butadiene rubber (BR), aluminum powder, and a mixture of aluminum nanopowders (NP) with boron in different ratios of Al/B components.

2. Materials

We used a mechanical mixture of Al/B NPs, which was prepared from the initial NPs of aluminum Alex and amorphous boron. The mean particle diameter for nanoaluminum Alex and boron was d = 90–100 and 210–240 nm, respectively. The specific surface area was S_{sp} = 15.5 m^2/g for Alex and 8.6 m^2/g for boron. Nanopowder Alex was obtained by the method of electric explosion of conductors in argon (Advanced powder technologies, Russia). According to the manufacturer's data, nanoaluminum contains 90 wt. % of the active material, and boron is 99.5 wt. %.

Compositions of Alex/B were made from initial powders of aluminum and boron in different ratios of Al and B (Table 1) per 1.0 gram of the mixture. To ensure a uniform distribution of particles in the metal-boron system, the powders were mixed for ~ 10 min.

Table 1. Powder systems based on NP aluminum and boron.

Sample	Component ratio (wt. %)		Content (wt. %)		Corresponding phase
	Alex	B	Al	B	
1	13.7	2.0	87.3	12.7	–
2	10.7	5.0	68.2	31.8	–
3	8.7	7.0	55.5	44.5	AlB_2
4	2.7	13.0	17.2	82.8	AlB_{12}

To study the ignition characteristics of propellant compositions, we prepared cylindrical samples of HEM containing ammonium perchlorate (AP) and butadiene rubber (BR) and 15.7 wt. % NP Al/B with different ratio of components. The base HEM composition contained 15.7 wt. % microsized aluminum with d = 10.6 μm and an active metal content of 98.5 wt. %.

3. Results and discussion

3.1. Ignition of HEM

The ignition characteristics of the HEM compositions were determined on an experimental bench that included a continuous CO_2-laser RLS-200 with a wavelength of 10.6 μm and maximum power of 200 W, power-supply unit, cooling system, and ignition parameter recording system. The diameter of the laser beam at the exit from the semitransparent mirror of the CO_2-laser was approximately equal to the diameter of the sample. The test HEM samples containing metal fuel were prepared (in the form of cylinders with the diameter of 10 mm and height of 30 mm) by continuous pressing with subsequent solidification in a drying oven. Prior to testing, the samples were cut into tablets of 5 mm in height. A detailed description of the experimental setup based on CO_2-laser is presented in [10]. The ignition delay time t_{ign} of HEMs was determined by the difference in the electrical signals of the photodiodes recording the initiation time of the sample (opening of the electromagnetic shutter) and the appearance of a flame near the end surface of the HEM sample. The temperature on the end surface of the sample during heating and ignition of the HEM was monitored with a Jade J530 SB thermal imaging camera. We varied the density of the heat flux falling on the end surface of the HEM sample in the range of q = 65–210 W/cm^2 to determine the critical conditions for the propellant ignition. The relative error in the measurement of the delay time data t_{ign} was equal to 5–10 % with a confidence of 0.95.

We determined the ignition delay time of the HEM compositions containing Alex/B vs. the heat flux density under radiant heating. Figure 1 depicts the measurement results as dots. The lines show the approximated dependences.

The obtained experimental dependences were fitted to a power function of the following form:

$$t_{ign} = A \cdot q^{-B}, \quad (1)$$

where t_{ign} is the ignition delay time of the HEM sample, ms; q is the heat flux density, W/m^2; and A, B are fitted constants.

Fitted constants and determination coefficient R^2 for the experimental data are given in Table 2.

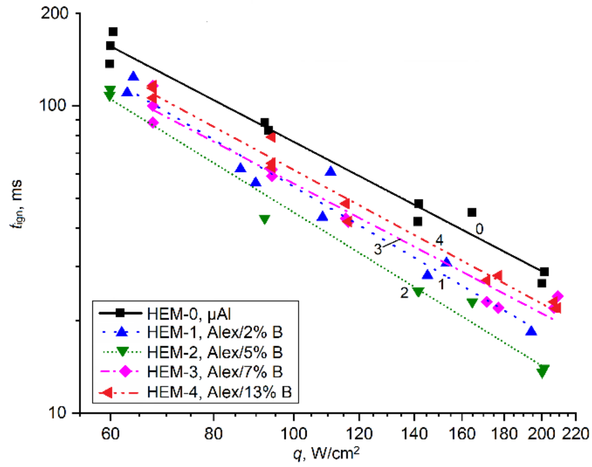

Figure 1. The ignition delay time of the HEM samples containing µAl and Al/B vs. the heat flux density.

Table 2. Fitted constants of eq. (1) and determination coefficient.

HEM sample	$A, \cdot 10^4$	B	R^2
HEM-0, µAl	4.78	1.39±0.12	0.97
HEM-1, Alex/2% B	7.73	1.58±0.17	0.94
HEM-2, Alex/5% B	9.28	1.66±0.11	0.98
HEM-3, Alex/7% B	3.58	1.40±0.14	0.95
HEM-4, Alex/13% B	4.82	1.45±0.09	0.98

The experimental results of the study depicted that using mechanical mixture of Alex/B in the propellant composition reduces the ignition delay time by 17–52% in the range of heat flux density q = 60–200 W/cm^2 in comparison with HEM-0 composition containing µAl (Figure 1). For the HEM-2 composition containing the Alex/5 % B, the ignition delay times t_{ign} have minimal values (33–52 % shorter compared to HEM-0). The using mechanical mixture of Alex/B in a ratio of 13.7/2.0, 8.7/7.0 and 2.7/13.0 wt. % in HEM t_{ign} are reduced by 22–37, 27–28, and 17–22%, respectively.

High-speed video recording frames show that the appearance of a flash near the end surface of the HEM sample occurs in the area of laser beam hot spots (maximum values of the heat flux), after which the flame zone grows in the axial and radial directions, covering the entire area of the sample end surface. When the flame appears, a sharp rise in temperature is observed on the propellant end surface due to additional radiation. An increase in temperature on the sample surface is associated with additional heat input from the gas-phase zone of chemical reactions and heat transfer due to convection and radiation, as well as additional heat release on the propellant surface during the oxidation of Alex particles. In the area of hot spots, a heating zone and a reaction layer are formed, which promotes pyrolysis and the outflow of gaseous decomposition products of propellant components from the end surface. After a short period, a glow area forms on the propellant surface, passing into the visible flame front in the gas phase. Depending on the heat flux density and the Alex/B content, the formation time of a visible flame on the HEM surface is ~ 15–30 ms. With a sharp increase in the temperature on the sample surface and the outflow rate of pyrolysis gases, we observe the output of burning particles of aluminum and boron. These particles are intensively oxidized in the chemical reaction zone with significant heat release. The process of forming a steady flame front near the propellant surface is long compared to t_{ign}, and amounts to ~ 300–400 ms.

Thus, the use of NP Alex/B with a mass content of boron from 13 to 32 % in the HEM composition increases the heating rate and formation of a reaction sample layer. It also promotes additional energy release at the moment of flame appearance near the sample surface due to an increase in the absorption capacity of the propellant surface and earlier ignition of nanosized aluminum particles.

3.2. Activation energy
To calculate the kinetic parameters of propellant ignition, we used the experimental data on the dependence of the ignition delay time on the heat flux density. The formal activation energy, the reaction heat effect, the pre-exponential factor and the ignition temperature of the HEM samples were determined by the method presented in [10]. In calculating the formal kinetics constants, we used the following thermophysical parameters of the propellant [10, 11]: density $\rho = 1.87$ g/cm^3, specific heat $c = 1.24$ kJ/(kg·K), and thermal conductivity $\lambda = 0.66$ W/(m·K). The calculation results are shown in Table 3.

Table 3. Calculation data of the formal kinetic parameters for the HEM samples.

HEM sample	E (kJ/mol)	Qz (W/g)	T_{ign0} (K)	T_{ign} (K) at q = 60–200 W/cm^2
HEM-0, μAl	54	$8.69\cdot10^{8}$	518	527–631
HEM-1, Alex/2% B	84	$4.42\cdot10^{12}$	486	496–555
HEM-2, Alex/5% B	108	$4.24\cdot10^{15}$	474	482–525
HEM-3, Alex/7% B	57	$5.17\cdot10^{9}$	477	490–575
HEM-4, Alex/13% B	61	$1.12\cdot10^{10}$	492	502–585

The HEM-2 sample containing Alex/5 % B has the highest activation energy E = 108 kJ/mol and reaction heat effect $Qz = 4.24\cdot10^{15}$ W/g, but HEM-2 sample has the minimum ignition temperatures over the entire range of changes in the heat flux density (see Table 3). Moreover, the use of NP Alex/B with different ratios of Al and B in the HEM reduces the propellant ignition temperature by 7–17 % compared to HEM-0, but increases the activation energy due to the oxidation of Alex particles on the propellant surface upon heating the HEM, which has the maximum value E = 119 kJ/mol [10].

Conclusions
As a result of the experimental study of the ignition characteristics of HEM compositions containing the oxidize AP, BR, and NP aluminum with boron, we have determined the effect of Alex/B-fuel on the values of the ignition delay time and ignition temperature and activation energy. With the use of high-speed video recording and thermal imaging, the main stages of HEM compositions ignition have been established.

It is shown that the use of Alex/B powder systems as part of HEM reduces the ignition delay times of propellant by 17–52% in the range of the heat flux density of 60–200 W/cm^2 in comparison with HEM containing microaluminum. The most effective is the HEM composition containing Alex/5% B, which has the shortest ignition time (33–52% shorter).

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