

Ignition of high-energy materials containing boron and aluminum diboride

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Abstract

Boron and its compounds are considered as possible high efficiency fuel for HEM. This work is aimed to modify a commercial 99.5% pure boron and AlB_2 powders to improve the ignition and combustion characteristics for solid propellants. The ignition parameters for the model HEM sample based on AP, AN and MPVT energetic binder, containing Al, B, and AlB_2 powders, are presented. It was found that the greatest effect at the laser ignition is achieved at a full replacement of Al by B powder, the ignition time and the activation energy of HEM are reduced by 2.1–2.7 and 1.8 times, respectively. Then the use of AlB_2 powder in HEM the ignition time is reduced by 1.7–2.4 times, and the activation energy is increased by 1.4 times.

1. Introduction

Boron and its compounds are considered as possible high efficiency fuel components of solid propellants for solid fuel rocket and ramjet engines [1–4]. Boron hydrides and organic derivatives have the high burning rates, which varying in a wide range at changing the air relation and pressure in the combustion chamber. The combustion heat of boron in the oxygen on 1 kg metal more than 1.9 times the combustion heat of aviation kerosene and aluminum.

Note that solid propellants are widely used, which contain up to 22 wt.% aluminum micron powder. According to the study [5, 6] the aluminum oxidation during the combustion of composite solid propellants strongly influence by the presence on the burning surface the refractory layer containing the aluminum oxide particles and carbonaceous residues. Melting point of alumina significantly above the melting point of aluminum. The aluminum particles combustion possible at the high temperature gradient of high-energy materials (HEMs) reaction layer near the burning surface with occurrence of cracks and destruction of the oxide layer resulting in the oxidation of active metal. It is well known [7] that the destruction of the aluminum oxide layer on the particle surface may react with the carbon particles to form aluminum carbide.

However, HEMs, containing aluminum micron powders, have a long delay ignition time and low burning rate compared to HEMs, containing ultrafine powders of aluminum or other metals [8, 9].

The aim of this work was to characterize the ignition and combustion of boron and AlB_2 powders in HEM and to determine the experimental dependences of the ignition time on heat flux, values of the ignition temperature and the activation energy for the model HEMs based on ammonium perchlorate and nitrate, energetic binder, containing the high-energy metal fuels.

2. Experimental

2.1 HEM samples

To study the main ignition characteristics we used three tested samples of HEM. The first is the basic composition, containing ammonium perchlorate AP (fraction with particle size 160–315 μm), ammonium nitrate AN (fractions with particle size less than 50 μm), the energetic binder of MPVT-ASP type, and 30 wt.% Al micron powder of ASD-4 type. In other tested compositions the Al powder is completely replaced by the amorphous boron and aluminum diboride powders (Fig. 1).

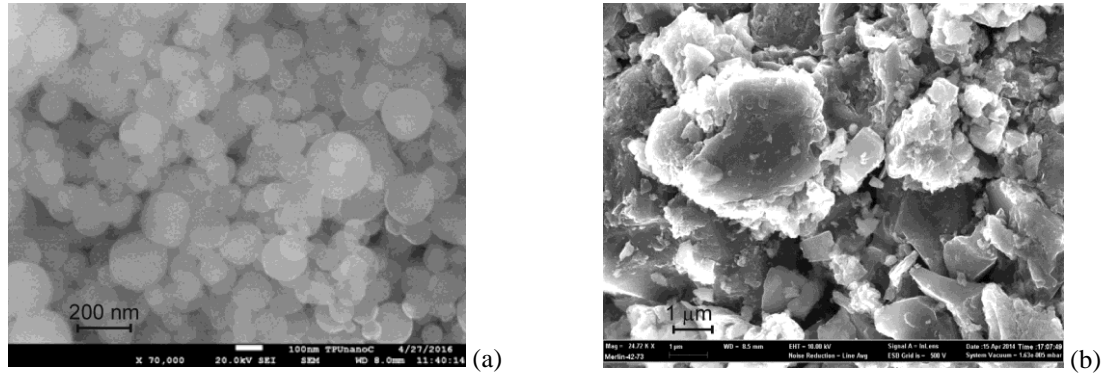


Figure 1: SEM images of amorphous boron (a) and aluminium diboride (b) powders.

According to the manufacturers data the original substance content in tested boron powder was 99.5 wt. % and the specific surface area comprised $8.63 \text{ m}^2/\text{g}$. Aluminum diboride was obtained by the conjugate SHS process. For the using AlB_2 powder the content of the target phases was 93 % and the mean particle size was 6.2 μm .

2.2 Ignition of HEM

The ignition process was studied with the use of setup for the radiant heating on the basis of continuous CO_2 -laser with the wavelength of 10.6 μm and power of 200 W (Fig. 2). Prior to testing the HEM samples were cut into tablets of 5 mm in height.

The test HEM sample (6) was attached to the substrate of recoil force transducer (8) to register the gasification products outflow from the burning surface. When opening the shutter (4) the radiation was focused by the sodium chloride lens (5) to the HEM sample (6). Signals from the recoil force transducer (8) and photodiodes (7) were transmitted to the L-card-E 14-440 ADC (9) and recorded in the personal computer (10), and then processed with the software application LGraph2. The HEM sample time delay of start gasification was determined as time interval between the moments of signals change of photodiode near the shutter (7) and the recoil force transducer (8). Photodiode (7) registered the moment of opening the shutter, transducer (8) recorded the appearance of recoil force signal of gasification products flowing from the HEM front (irradiated) sample surface. The ignition time t_{ign} of HEM was determined by difference between the moments of signals from two photodiodes (7), one of which registered the appearance of flame near the end surface of HEM sample. The relative error of ignition time measuring was equal 5–12 % at the value of confidence probability 0.9.

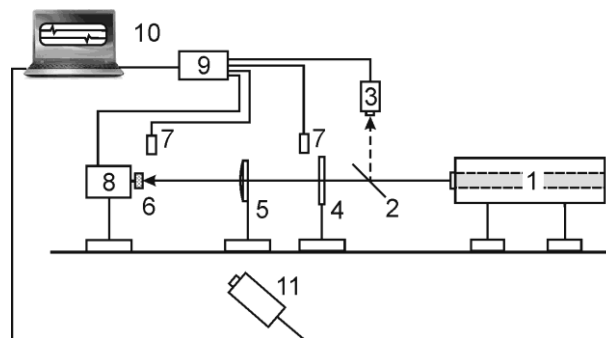


Figure 2: The scheme of experimental setup based on CO_2 -laser: 1 – CO_2 -laser; 2 – beam-splitting mirror; 3 – thermoelectric sensor of radiation power; 4 – shutter; 5 – lens; 6 – HEM sample; 7 – photodiodes; 8 – transducer; of recoil force; 9 – ADCs; 10 – PC; 11 – thermal imager.

The radiation power Q and heat flux q of CO_2 -laser beam was measured by the thermoelectric sensor of radiation power of Ophir FL400A type (3). The maximum radiation power was defined in the center of the laser beam using a diaphragm with diameter 2 mm. The diameter of the laser beam incident on a HEM sample surface was 10 mm.

3. Results and Discussion

The ignition time for tested HEM samples was determined in atmospheric conditions. The experimental dependences of HEM ignition time vs. the heat flux were determined (Fig. 3).

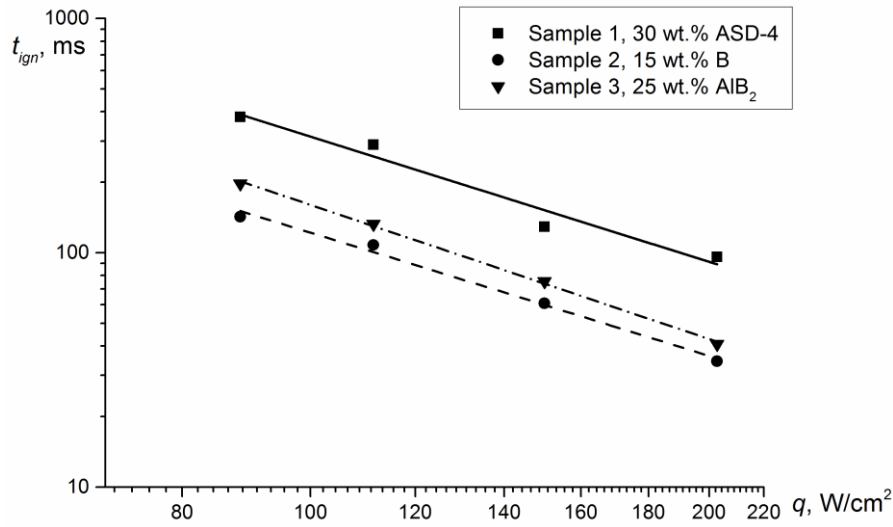


Figure 3: The ignition time vs. the heat flux for tested HEM samples containing metal powder:
 Al – $t_{ign}=9.90 \cdot 10^5 \cdot q^{-1.75}$; B – $t_{ign}=2.02 \cdot 10^5 \cdot q^{-1.61}$; AlB₂ – $t_{ign}=7.39 \cdot 10^5 \cdot q^{-1.83}$.

It was found that a complete replacement of micron aluminum by boron powder in HEM leads to a decrease of the ignition time by 2.1–2.7 times in the heat flux range of 90–200 W/cm². Replacement of aluminum by aluminum diboride micron powder in the HEM basic composition reduces the ignition time of sample by 1.7–2.4 times. The kinetic constants of HEM ignition were determined with the use and solution of equation [10]:

$$t_{ign} = 0.359 \left(1 - \frac{T_0}{T_{ign}} \right)^2 \frac{E_a c_p}{RQz} \exp \left(\frac{E_a}{RT_{ign}} \right),$$

where E_a is the activation energy, R is the universal gas constant, Q is the specific (per unit weight) heat of reaction, z is a pre-exponential factor, T_{ign} is the quasi-steady ignition temperature that is determined from the condition of equality between the rate of heat supply from reaction layer of chemical interactions and the rate of heat removal into the depth of condensed phase

$$T_{ign} = T_0 + 1.2q \sqrt{\frac{t_{ign}}{\lambda c_p \rho}},$$

λ , c_p , ρ are factors of the thermal conductivity, the specific heat capacity and the density for the HEM samples. The calculated kinetic constants and the measured ignition surface temperatures for tested HEM samples are presented in Table 1.

Table 1: The activation energy, specific heat of reaction, ignition temperature and surface temperature on the reaction layer for tested HEM.

Parameter	HEM sample containing metal powder		
	ASD-4	B	AlB ₂
E_a , kJ/mol	219	120	307
Qz , W/g	$8.32 \cdot 10^{10}$	$3.77 \cdot 10^8$	$4.81 \cdot 10^{18}$
T_{ign} , K	1203	859	935
\bar{T} , K	980±30	950±110	1005±90
T_{max} , K	1420±80	1530±120	1600±170

Here there are experimental values of the mean \bar{T} and the maximum T_{\max} surface temperatures on the HEM reaction layer during the heating and ignition (appearance of visible flame) which obtained using a thermal imager Jade J530 SB at $q = 115 \text{ W/cm}^2$ (Fig. 4).

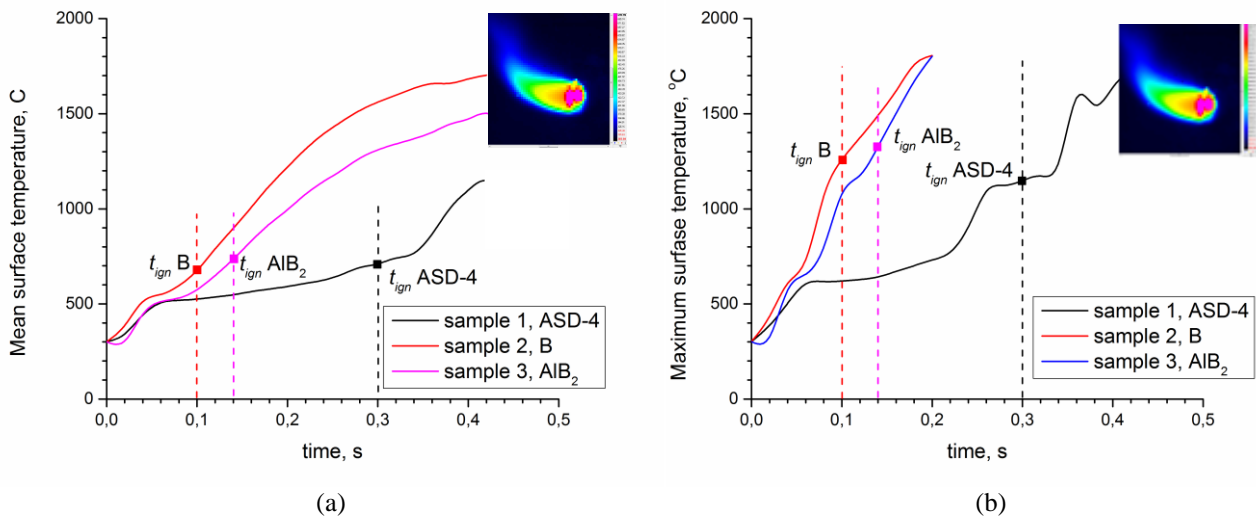


Figure 4: The mean (a) and the maximum (b) ignition surface temperatures for HEM samples at radiant heating.

The thermal imaging data showed that the surface temperatures of the tested samples are approximately the same in the moment of appearance of visible flame. Though the calculated quasi-steady ignition temperature of HEM is less by 344 K for sample with B powder and by 268 K for sample with AIB₂ powder in comparison with Al HEM sample. And the HEM activation energy is less by 99 kJ/mol for sample with B powder and is more by 88 kJ/mol for sample with AIB₂ powder. This is due to the different heating rate of HEM thermal layer and the oxidation mechanism of boron and AIB₂ particles during ignition and combustion of tested sample.

The boron particle combustion occurs in two stages [3]. Following heatup to about 950–1100 K, the boron particle is ignited and becomes luminous releasing a large amount of heat. During ignition stage the boron particle is coated by a molten boron oxide layer. According to experimental data (Table 1), the mean surface temperature is $\bar{T} = 950 \text{ K}$ and the maximum surface temperature is $T_{\max} = 1530 \text{ K}$ for HEM sample with boron powder in the moment of HEM appearance of visible flame. The melting point of boron oxide is 723 K and the boiling temperature is 2133 K. Ignition time of boron particle may be from 1.7 to 5.0 ms depending on the ambient temperature, oxygen concentration and particle size [11]. Oxygen must diffuse through this layer to react with the boron, in order to provide reaction heat for vaporization of the oxide layer. Before the full-fledged combustion stage can occur, the oxide layer must be completely removed from the boron particle. Provided the ambient temperature is sufficiently high, comes into a second stage of combustion.

The aluminum diboride particle combustion is not known well enough. Experimental data (Table 1) show that the mean surface temperature is 1005 K and the maximum surface temperature is 1600 K for HEM sample with AIB₂ powder and these temperatures are more than for HEM sample with boron or aluminum powder. In this case, the ignition time of HEM sample with AIB₂ powder is close to the ignition time of HEM sample with boron powder. Perhaps this is due to the formation of the boron oxide and alumina layer on the AIB₂ particle and its properties during the heating and ignition of HEM sample. It is require further study.

4. Conclusions

The ignition parameters for the HEM based on ammonium perchlorate, ammonium nitrate and energetic binder of MPVT-ASP type, containing powders of aluminum, amorphous boron and diboride aluminum are presented. It was found that the greatest effect at the laser ignition is achieved at a full replacement of Al micron powder by 99.5 % pure boron, at which the ignition time and the activation energy of HEM sample are reduced by 2.1–2.7 times and 1.8 time, respectively, in the heat flux range of 90–200 W/cm².

When replacing Al micron powder by AIB₂ powder in HEM the ignition time is reduced by 1.7–2.4 times, and the activation energy is increased by 1.4 times. The different heating rate of HEM thermal layer and the oxidation mechanism of boron and AIB₂ particles on the sample burning surface and in the gas phase zone during ignition and

combustion can improve the energetic characteristics of HEM in the propulsion systems in comparison with aluminized solid propellants.

Acknowledgment

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