

Thermal analysis and ignition of HEM containing aluminum and titanium borides

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Abstract. This paper describes the data of oxidation kinetics for metal fuels and ignition characteristics for the high-energy material (HEM) samples based on ammonium perchlorate, ammonium nitrate and an energetic binder, containing the powders of Al, B, AlB₂, AlB₁₂ and TiB₂. The thermal oxidation of metal fuels and the thermal decomposition of the HEM samples were determined using a combined Netzsch STA 449 F3 Jupiter analyzer. The ignition of the HEM samples was studied using the radiant heating setup based on continuous CO₂ laser in the heat flux density range of 90–200 W/cm². Experimentally it was found that the complete replacement of aluminum powder by amorphous boron in the HEM sample significantly reduces the ignition delay time (by 2.2–2.8 times) in the same heat flux density. The ignition delay time of the HEM sample containing titanium diboride powder decreases slightly (by 10–25%) relative to the ignition delay time of the Al-based HEM.

1. Introduction

Boron is an attractive element for incorporation in energetic materials because it offers a good combination of high heating value and density. The calorific and volumetric heating value for boron is 58 kJ/g and 136 kJ/cm³ representing an 87 and 62% increase over aluminum (31 kJ/g and 84 kJ/cm³), respectively [1]. However, boron is not commonly used in propulsion applications and other energetic material applications due to limitations. The primary limitations are the ignition and complete combustion of boron particles. Boron has high melting and boiling points of 2075 and 3658 °C. In addition, boron particles have long ignition and combustion times due to the formation of an inert oxide layer on the particle surface, which prevents the diffusion of the oxidizer to pure boron. This oxide coating has a low melting and boiling temperatures (450 and 1860 °C [2, 3]) in comparison with pure boron. In this case, the oxide agglomerate can create larger particles that may not burn completely during combustion. As a result, boron particles are difficult to ignite and complete combustion [4].

One of the ways to intensify the ignition and combustion processes of boron in the combustion chamber is the use of inflammable and quick-burning metals, which can be used as mechanical mixtures or alloys. The use of metal/boron composites, for example, Al/B, Mg/B, Mg/Al/B, Zn/B, Fe/B, Cu/B, or their oxides contributes to the acceleration of boron oxidation, significantly reduces the ignition delay time and increases the combustion completeness of fuel particles [5, 6]. Borides of aluminum, titanium, and magnesium are particular interest and can be used as high-energy component for composite solid propellants and hybrid fuels due to their high heat of combustion (at the level of boron) and better inflammableness [7, 8].



This paper presents the experimental data of the thermal analysis and ignition of the high-energy material (HEM) samples based on double oxidizer, an energetic binder, containing micron metal powders of aluminum borides AlB_2 and AlB_{12} , titanium boride TiB_2 , obtained using SHS, as well as aluminum and amorphous boron.

2. Materials and Methods

2.1. The HEM sample

We studied the HEM samples based on ammonium perchlorate AP (15 wt. %, fractions with particle size less than 50 μm and 160–315 μm in the ratio of 40/60), ammonium nitrate (AN) (35 wt. %, a fraction less than 100 μm), MPVT energetic binder (20 wt. %), and Al powder (30 wt. %, spherical micron powder). In the other fourth HEM samples, the Al powder was completely replaced by the powder of amorphous boron, aluminum diboride AlB_2 , aluminum dodecaboride AlB_{12} , or titanium diboride TiB_2 (Fig. 1). Metal borides were obtained by SHS in Laboratory of High Energy Systems and New Technologies at Tomsk State University. The sintered pressed metal samples were milled in a ball mill. In AlB_2 and AlB_{12} powders, the content of aluminum and boron was 55.5 wt.% Al and 44.5 wt.% B, and 17.2 wt.% Al and 82.8 wt.% B, respectively, as measured in the X-ray diffractometer. In TiB_2 powder, the content of titanium and boron was 68.9 wt.% Ti and 31.1 wt.% B. According to the manufacturer the content of active Al in aluminum powder was 98.5 wt.% and 99 wt.% active B in amorphous boron powder.

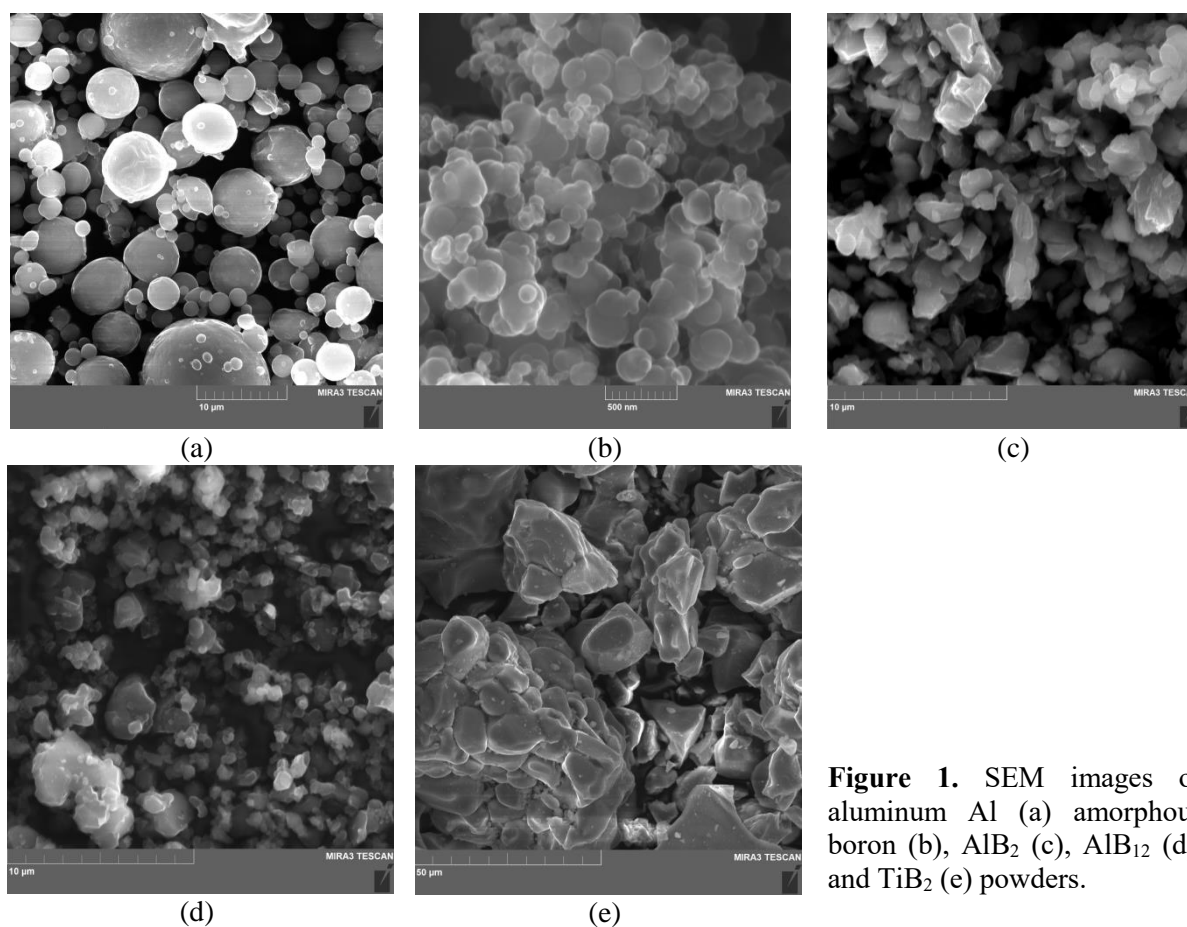


Figure 1. SEM images of aluminum Al (a) amorphous boron (b), AlB_2 (c), AlB_{12} (d), and TiB_2 (e) powders.

Particle size distribution measurements using the laser analyzer Analysette 22 showed that the average diameter of the tested metal powders was $d = 10.8 \mu\text{m}$ for Al powder, for amorphous boron

$d = 2.0 \mu\text{m}$, aluminum diboride AlB_2 $d = 6.2 \mu\text{m}$, aluminum dodecaboride AlB_{12} $d = 2.3 \mu\text{m}$ and titanium boride TiB_2 $d_{43} = 54.5 \mu\text{m}$.

2.2. Thermal analysis

The chemical activity of metal powders and thermal decomposition of the HEM samples were determined using the TG and DSC analysis at heating samples in a furnace at a constant rate. We used a combined analyzer Netzsch STA 449 F3 Jupiter. A ceramic crucible with a powder or cured HEM samples weighing of $\sim 10 \text{ mg}$ was placed in a furnace. The metal powders were heated from 30 to 1400°C in air at a constant heating rate of $20^\circ\text{C}/\text{min}$. In case of HEM, the samples were heated in argon at $10^\circ\text{C}/\text{min}$.

2.3. Ignition method

The ignition of the HEM samples was studied with the use of RLS-200 continuous CO_2 laser with the wavelength of $10.6 \mu\text{m}$, beam diameter of 10 mm and power of 200 W . A detailed description of the experimental setup based on CO_2 laser is presented in [9]. The HEM samples were cut into tablets of 5 mm in height. The flat end surface of the sample was visually monitored for the absence of pores, depressions and cracks. The sample was fixed on a holder. When the electromagnetic shutter was opened, a radiant heat flux fell on the HEM surface and ignited it. The moment of ignition of the HEM sample was recorded by the appearance of a flame near the sample surface by a photodiode.

3. Results and discussion

3.1. Thermal analysis data

Data of thermal oxidation for metal and boron powders and decomposition for the HEM samples were obtained. The TG and DSC curves are presented in Figure 2 for the Al-, B-, AlB_2 -, AlB_{12} - and TiB_2 -based HEM samples (2a, 2b) and tested metal powders (2c, 2d).

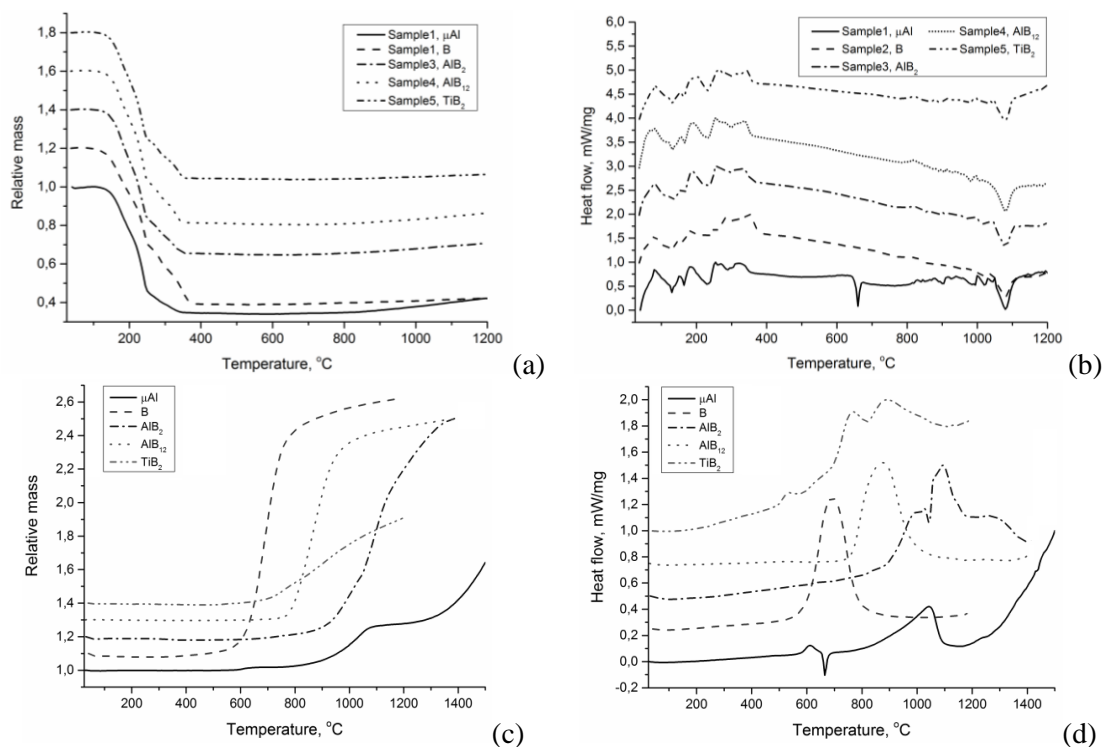


Figure 2. TG and DSC curves of the HEM samples (a, b) and metal powders (c, d).

The values of the onset, intensive and end decomposition temperatures, and the maximum decomposition rate of the HEM samples are shown in Table 1. The start of the decomposition process of HEM corresponds to a 10% change in the mass of the sample from the initial mass. We determined the values of the onset, intensive and end oxidation temperatures, the weight gain, and the maximum oxidation rate of the tested metal powders (Table 2).

Table 1. Decomposition temperatures and maximum decomposition rate of the HEM samples, containing metal powders.

HEM sample	$T_{on}, ^\circ\text{C}$	$T_{int}, ^\circ\text{C}$	$T_{end}, ^\circ\text{C}$	Maximum decomposition rate, $v_{dec}, \text{mg/s}$ (at T range, $^\circ\text{C}$)
Sample 1, Al	170	225	350	0.00699 (229 – 240)
Sample 2, B	162	237	387	0.0064 (232 – 242)
Sample 3, AlB ₂	167	222	357	0.00695 (227 – 237)
Sample 4, AlB ₁₂	167	227	356	0.0081 (232 – 240)
Sample 5, TiB ₂	167	228	357	0.0068 (227 – 240)

Table 2. Oxidation temperatures, weight gain, and maximum oxidation rate of metal powders.

Me powder	$T_{on}, ^\circ\text{C}$	$T_{int}, ^\circ\text{C}$	$T_{end}, ^\circ\text{C}$	Weight gain $\Delta m, \%$			Maximum oxidation rate, $v_{ox}, \text{mg/s}$ (at T range, $^\circ\text{C}$)
				400 – 660 $^\circ\text{C}$	660 – 1400 $^\circ\text{C}$	400 – 1400 $^\circ\text{C}$	
Al	580	1044	1088	1.9	26.1	28.0	0.0032 (1015 – 1050)
B	605	693	778	40.7	112.8	153.5	0.0056 (1475 – 1495)
AlB ₂	901	1094	1397	0.9	131.7	132.6	0.0199 (661 – 711)
AlB ₁₂	764	875	976	0.5	128.4	128.9	0.0089 (1077 – 1107)
TiB ₂	495	768	1094	2.2	49.3	51.5	0.014 (829 – 894)
							0.0026 (855 – 940)

The thermal analysis data showed that the HEM samples begin to react at a temperature of ~ 100 – 120 $^\circ\text{C}$ due to the onset of the polymer energetic binder decomposition. In the temperature range of 210 – 250 $^\circ\text{C}$ the chemical reaction rate during the decomposition of HEM components increases and reaches maximum values due to the onset of oxidizer decomposition (AP and AN). All exothermic and endothermic reactions of the HEM samples decomposition take place up to 400 $^\circ\text{C}$, while metal fuels are oxidized at temperatures above 600 – 700 $^\circ\text{C}$. According to Table 1 the highest decomposition rate is 0.008 mg/s for the AlB₁₂-based HEM sample, the smallest decomposition rate is 0.0064 mg/s for the B-based HEM sample.

The oxidation onset of Al powder begins in the temperature range of 580 – 640 $^\circ\text{C}$ with insignificant heat release (Figure 2c). It can indicate the possible formation of oxide layer cracks on the particle surface and the oxidation of aluminum in contact with air. The endothermic melting of aluminum occurs at a temperature of 660 $^\circ\text{C}$, which is accompanied by the weight gain of the Al powder due to the formation of aluminum oxide Al₂O₃ on the particle surface. The weight gain of the Al powder is 26% in the temperature range of 800 – 1090 $^\circ\text{C}$ with a maximum heat release at 1044 $^\circ\text{C}$. Oxidation of aluminum takes place in two stages. Second oxidation stage of Al is followed a sharp weight gain of

powder upon heating above 1200 °C. With an increase in temperature to 1475 °C, the oxidation rate becomes maximum. The oxidation of other boron-metal powders takes place in a single stage with the lower temperatures compared to Al powder. The oxidation temperatures and the weight gain of B, AlB₂, AlB₁₂, and TiB₂ powders are presented in Table 2.

We determined the maximum oxidation rate of the metal powders. The highest oxidation rates are observed for amorphous boron powder ($v_{\text{ox}} = 0.0199$ mg/s) and aluminum dodecaboride ($v_{\text{ox}} = 0.014$ mg/s), the smallest oxidation rate is observed for TiB₂ ($v_{\text{ox}} = 0.0026$ mg/s) due to the presence of coarse particles and small specific surface area.

3.2. Ignition delay time

The ignition delay time of the HEM samples vs. the heat flux density dependences were determined (Figure 3).

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

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

where t_{ign} is the ignition delay time of the HEM sample, ms; q is the heat flux density, W/m²; A , B are fitted constants.

Fitted constants and determination coefficient R^2 for the experimental data are given in Table 3.

Table 3. Fitted constants of eq. (1) and determination coefficient.

HEM sample	$A, \cdot 10^5$	B	R^2
Sample 1, Al	9.90	1.75	0.96
Sample 2, B	2.02	1.61	0.98
Sample 3, AlB ₂	1.78	1.53	0.87
Sample 4, AlB ₁₂	7.39	1.83	0.99
Sample 5, TiB ₂	4.71	1.62	0.99

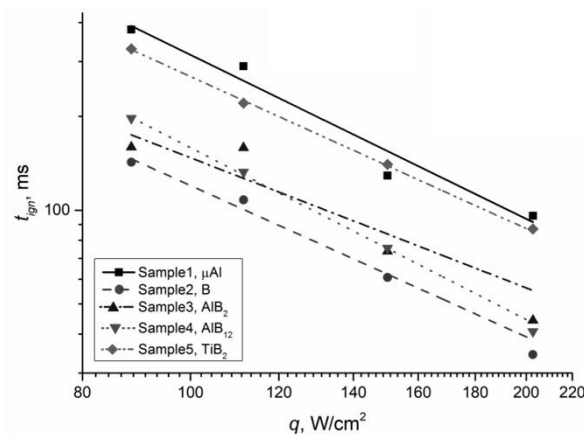


Figure 3. The ignition time of the HEM samples vs. the heat flux density.

Experimentally it was found that a replace of aluminum powder by amorphous boron or aluminum borides AlB₂ and AlB₁₂ in the HEM composition significantly decreases the ignition delay time by 2.2–2.8 and 1.7–2.2 times, respectively, in the heat flux density range of 90–200 W/cm². The difference between the ignition delay time of the HEM samples with TiB₂ and Al powders is insignificant and amounts to 10–25%.

Conclusions

This study presents the effect of boron or metal borides powders AlB_2 , AlB_{12} and TiB_2 on the thermal decomposition and ignition characteristics of the HEM samples based on AP, AN and energetic binder.

We determined that decomposition of the HEM samples begins at a temperature of $\sim 100\text{--}120^\circ\text{C}$ due to the onset of the polymer binder decomposition. The maximum rate of chemical reaction for HEM is obtained in the temperature range of $220\text{--}240^\circ\text{C}$ during the combined decomposition of oxidizer and binder. The metal fuel oxidation begins at temperatures above 600°C . With an increase in the concentration of boron in aluminum boride, the oxidation temperature decreases and the oxidation rate increases.

The oxidation onset temperature of the Al, AlB_2 , AlB_{12} , and TiB_2 powders varies from 495 to 900°C and depends on the particle size and concentration of boron in metal alloy. The lowest intense oxidation temperature was obtained for titanium diboride. The maximum oxidation rate $v_{\text{ox}} = 0.014\text{ mg/s}$ was for AlB_{12} powder in the temperature range of $829\text{--}894^\circ\text{C}$ and for amorphous boron 0.0199 mg/s in $T = 661\text{--}711^\circ\text{C}$.

The complete replacement of aluminum powder with aluminum borides in the HEM sample leads to 1.7–2.2 times decrease in the ignition delay time in the range of heat flux density of $90\text{--}200\text{ W/cm}^2$. The ignition delay time decreased by 2.2 – 2.8 times by using amorphous boron in the HEM sample compared with the Al-based HEM sample. The presence of TiB_2 powder in the HEM sample leads to a slight decrease in the ignition delay time by 10–25 %.

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