Combustion and agglomeration of aluminized high-energy compositions

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Abstract. The results of combustion study for high-energy compositions (HECs) based on ammonium perchlorate (AP), butadiene rubber and ultrafine powder (UFP) aluminum Alex, and agglomeration of metal particles on the burning surface and composition of condensed combustion products (CCPs) are presented. It was found that partial replacement 2 wt. % of Alex by iron UFP in HEC increases the burning rate 1.3–1.4 times at the range of nitrogen pressure 2.0–7.5 MPa and reduces the mean diameter of CCPs particles d_{43} from 37.4 µm to 33.5 µm at pressure ~4 MPa. Upon partial replacement 2 wt. % of Alex by boron UFP in HEC the recoil force of gasification products outflow from burning surface is increased by 9 % and the burning rate of HEC does not change in the above pressure range, while the mean diameter of CCPs particles is reduced to 32.6 µm at $p \sim 4$ MPa.

1. Introduction

The modern high-energy compositions (HECs) contain as the oxidizer crystals of ammonium perchlorate (AP), ammonium nitrate (AN) and nitramines (RDX, HMX, CL-20) [1–2], combustible-binder – inert or energetic polymer rubber, and metal fuel – aluminum powder with typical content up to 22 wt. % [3–5]. These systems are used as the energy source of solid rocket motors and gas generators for various purposes. Adjustment of the HEC burning rate is mainly achieved by introduction in propellant formulation the catalysts, through partial or complete replacement of AP and AN by nitramines, by changes of the excess oxidizer factor, as well as the changing of the particle size of oxidizer and metal powders.

As the burning catalysts of HECs metal oxides: MnO_2, Ni_2O_3, Cr_2O_3, MgO, Fe_2O_3, Co_2O_3, CuO, SiO_2, copper, iron, zinc, cadmium and magnesium salts of chromic and metachromic acids, complex cyanides of copper, iron and nickel are used [6–9]. The most common and versatile in this group of catalysts are the systems containing copper, chromium, boron and iron [10–12].

This paper presents the experimental results on combustion processes of HECs based on aluminum ultrafine powder (UFP) Alex, containing additives of iron and amorphous boron UFPs and the methods for determine of parameters: the recoil force of gasification products outflow, the burning rate of samples, and the quantitative and phase compositions, the size distribution of particles of condensed combustion products (CCPs).

2. Experimental

2.1 The HEC samples

We studied the samples of HEC on the basis of bidispersed AP (fraction less than 50 μm and 160–315 μm in the ratio 40/60), inert combustible-binder (19.7 wt. %) – butadiene rubber plasticized by transformer oil, and aluminum UFP Alex (15.7 wt. %) obtained in argon using electric explosion of conductors with a shelf life of more than two years. In the second and third compositions of HECs 2 wt. % of the Alex UFP was partially replaced by 2 wt. % catalyst additives – UFPs of iron and amorphous boron. According to the measurements on the BET analyzer Nova 2200e in nitrogen the specific surface area of Alex amounts to 7.04 m^2/g, iron – 1.08 m^2/g, amorphous boron – 8.63 m^2/g. The studied cylindrical samples of HECs in diameter 10 mm and height 30 mm produced in the laboratory by extrusion pressing with the subsequent curing. The density of solid samples depending on the component composition was in an interval of 1.53–1.59 g/cm^3.

2.2 Combustion of HECs

The study of effect of iron and amorphous boron UFPs additives on the combustion process of HECs was carried in blow-through sampling bomb in nitrogen at different pressures [14]. We used the HEC samples in diameter 10 mm and height 25–30 mm in experiments with sampling of condensed combustion products (CCP). The lateral surface of samples was inhibited by heat resistant rubber «solpren» (a styrene/butadiene copolymer). During combustion of solpren the carbonaceous particles were formed, the contents of which in CCPs was not exceed 1 wt. %.

The burning rate of HECs was evaluated by known length and the burning time of samples, defined by a signal from a pressure sensor in bomb during the combustion. During combustion of HEC sample the gaseous and condensed combustion products passed through the metal sieve mesh packet and analytical aerosol filter which are captured solid particles of different sizes. Sampled CCP particles were divided onto four fractions – less than 80 μm, 80–160 μm, 160–315 μm and greater than 315 μm, and then subjected to a visual inspection, particle size and phase analyses.

The value of recoil force of gasification products outflow from the end surface of HEC sample during the heating of reaction layer, ignition and combustion of HECs was determined using recoil force transducer [13].

3. Results and discussion

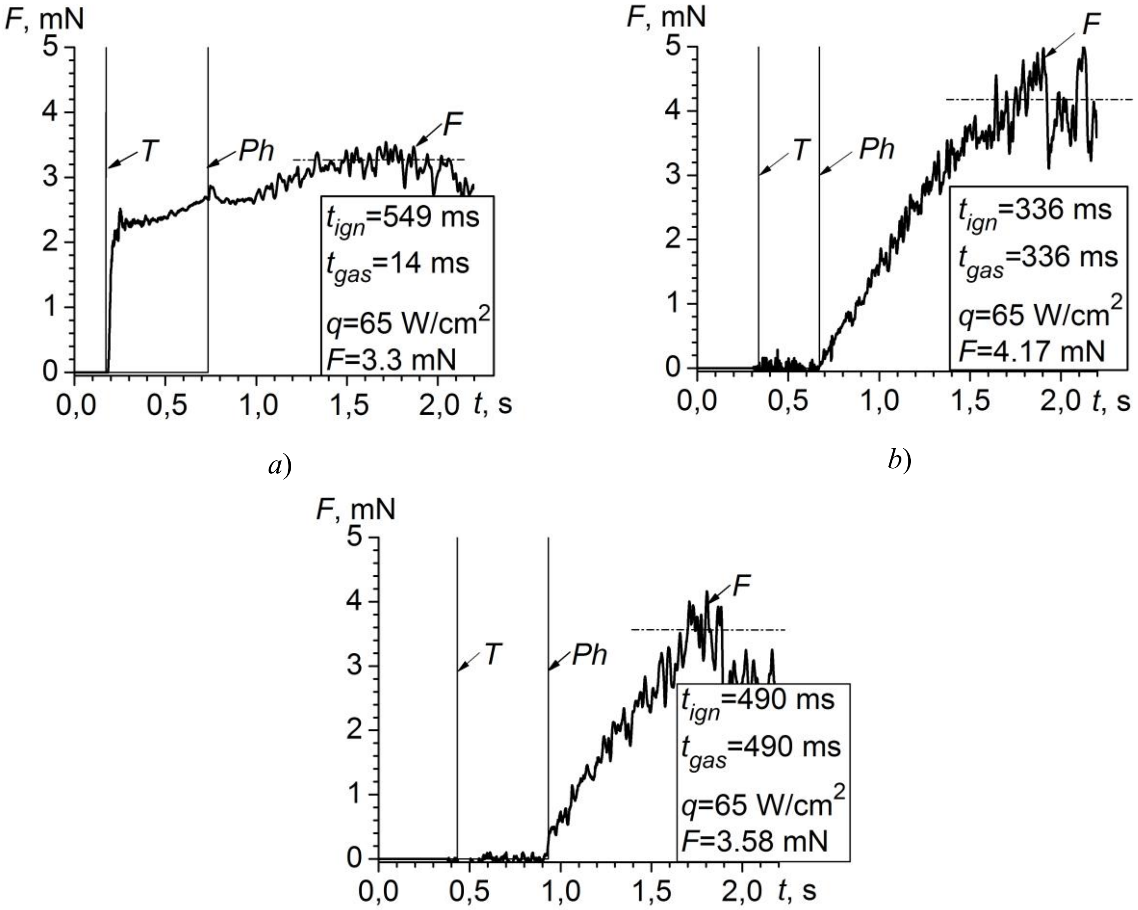
3.1 The recoil force

The values of the time of gasification and ignition, the recoil force of gasification products outflow for the solid propellants samples under study in atmospheric conditions were determined in air under normal conditions. Processing of signal recording from the recoil force transducer we get the value of recoil force F outflow of gasification products from the burning surface of HEC samples. Examples of records are shown in Figure 1.

Partial replacement of Alex by iron UFP in HEC leads to the increase of the recoil force of gasification products outflow from burning surface 1.3 times in the period of stationary combustion of HECs. For the partial replacement of Alex by boron UFP in the HEC composition the recoil force of gasification products outflow increases 1.1 times.

3.2 The burning rate

The values of the burning rate at different nitrogen pressures were determined in the sampling bomb (Figure 2). The values of the HECs burning rate and the relative mass of CCPs m_{ccp} equal to the ratio of the CCPs mass M_{ccp} to the mass of HEC sample M_{samp} at pressure ~ 4 MPa are presented in Table 1.



a) *b*)

c)

Figure 1. The signals of thermocouple (*T*), photodiode (*Ph*) and the recoil force transducer (*F*) that have been recorded over time interval embracing the heating, ignition and combustion processes for HECs samples with Alex (*a*), Alex+Fe (*b*) и Alex+B (*c*).

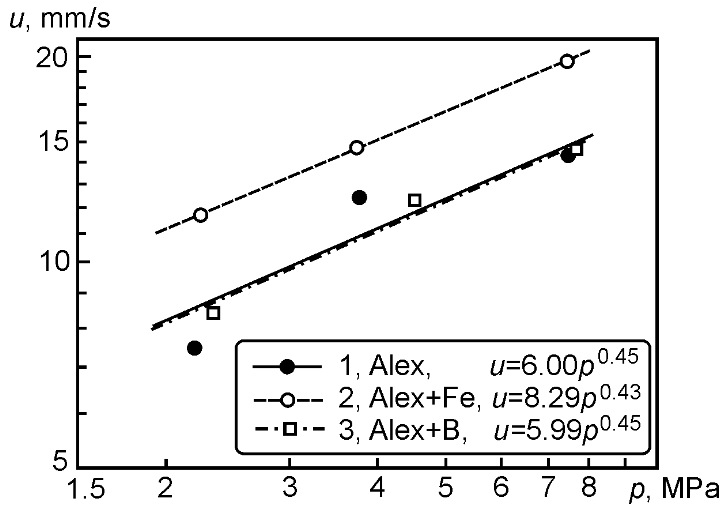


Figure 2. The burning rate of aluminized HECs from pressure.

Table 1. The burning rate of HECs and relative mass of CCPs at $p \sim 4$ MPa.

HEC sample	u (mm/s)	$m_{ccp} = M_{ccp}/M_{samp}$
1, Alex	12.4 ± 0.2	0.30 ± 0.04
2, Alex+Fe	14.7 ± 0.2	0.29 ± 0.03
3, Alex + B	12.3 ± 0.3	0.29 ± 0.04

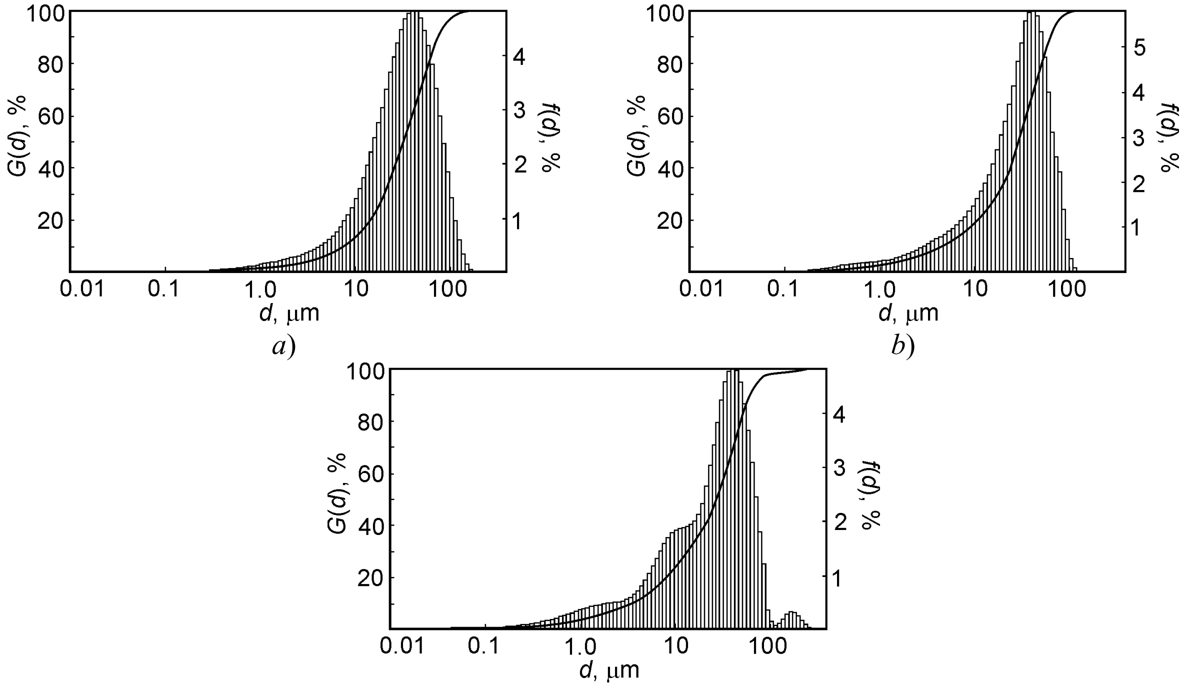
Partial replacement of Alex by iron UFP in HEC composition slightly decreases the exponent of burning rate law from 0.45 to 0.43 and the increase of the burning rate from 7.5 to 11.7 mm/s at pressure 2.2 MPa and from 14.3 to 19.7 mm/s at pressure 7.5 MPa. The mass of sampled CCPs of tested HECs practically does not change at nitrogen pressure ~ 4 MPa.

For partial replacement of Alex by boron UFP in HEC the burning rate and relative mass of CCPs at pressure ~ 4 MPa are virtually unchanged. The burning rates of HECs with Alex+B are equal 8.4 mm/s at pressure 2.3 MPa and 14.6 mm/s at pressure 7.7 MPa.

Obtained data of the HECs burning rate correlates well with the data of recoil force of gasification products outflow from burning surface of samples (see Figure 1).

3.3 Compositions of CCPs

Sampled CCPs at nitrogen pressure ~4 MPa were subjected to particle size and X-ray diffraction (XRD) analyses. The mass-size distribution function of CCPs particles measured with use of Analysette 22 particle size analyzer in distilled water under the ultrasound action are presented in Figure 3.



a)

b)

c)

Figure 3. Differential and cumulative mass size distribution function for CCP particles of aluminized HECs with Alex (*a*), Alex+Fe (*b*) and Alex+B (*c*).

Particle size measurements showed that the mass fraction of CCPs particle fraction less than 10 μm amounted 0.16, 0.18 and 0.27, for HECs with Alex, Alex+Fe and Alex+B, respectively, the particle fraction of CCPs less than 45 μm – 0.67, 0.71, 0.74, the particle fraction of CCPs less than 100 μm – 0.97, 0.99 and 0.98.

Partial replacement of Alex by iron UFP in the HEC composition decreases the mean particle diameter d_{43} from 37.4 to 33.5 μm. Partial replacement of Alex by boron UFP in HEC leads to the decrease of the CCPs d_{43} to 32.6 μm.

XRD analysis of CCPs performed using the Shimadzu XRD 6000 diffractometer showed that the content of amorphous phase in the sampled CCPs in the case of propellant with Alex is equal 18 wt. %, in the case of propellant with Alex+Fe – 22 wt. % and in the case of propellant with Alex+B – 26 wt. %. The phase composition of CCPs, sampled at nitrogen pressure ~ 4 MPa, is presented in Table 2.

Table 2. The phase composition (without the amorphous phase) of CCPs of aluminized HECs.

HEC sample	Content of phases in CCPs (wt. %)				
	α-Al_2O_3	θ-Al_2O_3	γ-Al_2O_3	AlN	C_3N_4
1, Alex	7.1	66.7	2.0	7.1	17.1
2, Alex+Fe	9.4	54.7	1.6	8.3	26.0
3, Alex+B	43.3	–	–	–	56.7

It was found that partial replacement Alex by Fe UFP in HEC increases the content of alumina α-Al_2O_3 (corundum) by 2.3 wt. %, aluminum nitride AlN – by 1.2 wt. %, carbon nitride C_3N_4 – by 8.9 wt. % and reduces the content of alumina θ-Al_2O_3 (monoclinic) by 12 wt. % in composition of sampled CCPs due to possible the catalytic effect, which reduces the temperature of the beginning of AP high temperature decomposition in the reaction layer of HEC, and the increase of the temperature in gas phase zone of chemical reactions, and also the exothermic reaction of iron and aluminum particles on the reaction layer near the surface of HEC sample.

Partial replacement of Alex by boron UFP in HEC increases the content of alumina α-Al_2O_3 by 6.1 times and carbon nitride C_3N_4 by 3.3 times in composition of sampled CCPs due to the possible increase of the heat release during combustion of boron UFP and, respectively, the temperature in the gas phase zone of chemical reactions.

4. Conclusions

The effects of additives of iron and amorphous boron UFPs in high-energy compositions on the basis of AP, butadiene rubber and 15.7 wt. % of aluminum Alex UFP on combustion characteristics were studied. Burning rate law and condensed combustion products were studied with use of a special designed blow-through sampling bomb at nitrogen pressure from 2.0 to 7.5 MPa.

It was found that partial replacement 2 wt. % of Alex by iron UFP in HEC increases of the recoil force of gasification products outflow from burning surface 1.3 times in the period of stationary combustion of samples and increases the burning rate 1.3–1.4 times at the range of nitrogen pressure 2.0–7.5 MPa and reduces of the mean diameter d_{43} of CCP particles from 37.4 μm to 33.5 μm at nitrogen pressure ~4 MPa. In the sampled combustion products at ~4 MPa the content of aluminum oxide α-Al_2O_3 is increased by 2.3 wt. %, aluminum nitride AlN – by 1.2 wt. % and carbon nitride C_3N_4 – by 8.9 wt. % due to possible the catalytic effect, which reduces the temperature of the beginning of AP high temperature decomposition in the reaction layer of HEC, and interaction of thermite mixture of aluminum and iron particles on the surface of the reaction layer of sample, and also the increase of the temperature in the gas phase zone of chemical reactions.

Partial replacement 2 wt. % of Alex by amorphous boron UFP in HEC increase of the recoil force of gasification products outflow from the burning surface 1.1 times. In this the burning rate of HEC does not change at the range of pressure 2.0–7.5 MPa, the mean diameter d_{43} of CCPs particles is reduced to 32.6 μm at pressure ~4 MPa, and the content of alumina α-Al_2O_3 and carbon nitride C_3N_4 are increased 6.1 times and 3.3 times in CCPs due to the possible increase of the heat release during combustion of boron UFP and the temperature in the condensed and gas phase zone of chemical reactions.

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