Influence of metals on ignition and combustion of composite solid propellants

*Alexander Korotkikh***, Vladimir Arkhipov*, Alexander Kiskin***, Oleg Glotov***, Konstantin Slyusarskiy**, Zhukov A.S.*, Promakhov V.V. **

**Research Institute of Applied Mathematics and Mechanics, Tomsk State University*

36, Lenin Ave., Tomsk, 634050, Russia

***Institute of Power Engineering, Tomsk Polytechnic University*

30, Lenin Ave., Tomsk, 634050, Russia

****Institute of Chemical Kinetics and Combustion SB RAS*

3, Institutskaya Str., Novosibirsk, 630090, Russia

Abstract

The paper presents measurement techniques for the recoil force, gasification time of products outflow from burning surface, burning rate of composite solid propellants (CSPs) with sampling of condensed combustion products (CCPs) to determine their size distribution, chemical and phase compositions, as well as the experimental study results of ignition and combustion of CSPs based on AP, an inert binder and aluminum ultrafine powder (UFP) type Alex, containing additives of iron and boron. It was found that the partial replacement 2 wt. % f Alex by iron UFP in CSP decreases the ignition time 1.3–1.9 times under initiation by CO_2-laser in the air at the range of heat flux density 55–220 W/cm^2 and increases the recoil force of gasification products outflow by 27 % in the period of stationary combustion and increases the burning rate 1.3–1.4 times at the range of nitrogen pressure 2.0–7.5 MPa. At the partial replacement 2 wt. % of Alex by boron UFP in CSP the ignition times are decreased 1.2–1.4 times, the recoil force of gasification products outflow is increased by 9 % and the burning rate of CSP does not change in the above pressure range.

1. Introduction

The modern composite solid propellants (CSPs) 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 CSP 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 CSPs 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 ignition and combustion processes of CSPs based on aluminum ultrafine powder (UFP) Alex, containing additives of iron and amorphous boron UFPs and the methods for determining the set of ignition and combustion parameters: the gasification and ignition times, 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 CSP samples

We studied the samples of CSP on the basis of bidisperse 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 CSPs 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 CSPs 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. Ignition of CSPs

The ignition study of CSPs was carried with the use of set up for the radiant heating on the basis of CO_2-laser with the wavelength of 10.6 μm and maximal power of 100 W (Fig. 1). Prior to testing the CSP samples were cut into tablets of 5 mm in height. The CSP samples were placed in the hollow cylinder of 10 mm depth made of ebonite for inhibiting the lateral surface and making one-dimensional flow of gasification products.

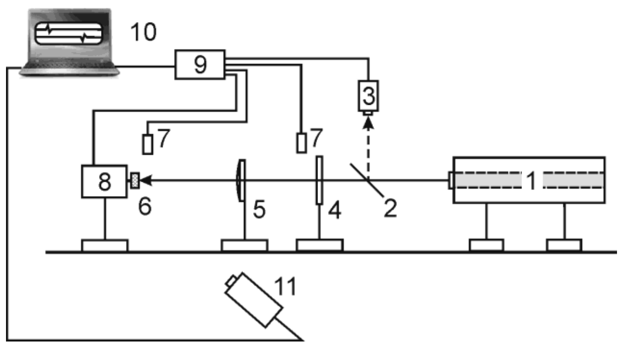

Figure 1: The scheme of experimental setup based on CO_2-laser: 1 – CO_2-laser; 2 – beam-splitting mirror; 3 – thermoelectric sensor of radiation power; 4 – shutter; 5 – lens; 6 – CSP sample; 7 – photodiodes; 8 – transducer of recoil force; 9 – ADCs; 10 – PC; 11 – video camera

The test CSP 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 CSP 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 time delay of start gasification t_{gas} of CSP sample was determined as time interval between the moments of signals change of photodiode near the shutter (7) (or a thermocouple installed in the laser beam behind the shutter), 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 front (irradiated) sample surface. The ignition times of CSPs 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 CSP sample. The relative error of delay times measuring of gasification t_{gas} and ignition t_{ign} was equal 5–12 % at the value of confidence probability 0.9.
The value of recoil force of gasification products outflow from the end surface of CSP sample during the heating of reaction layer, ignition and combustion of CSPs was determined using recoil force transducer [13].
The power of laser radiation was measured by the thermoelectric sensor of radiation power (3). The maximum radiation power was defined in the center of the laser beam.

2.3. Combustion of CSPs

The study of effect of iron and amorphous boron UFPs additives on the combustion process of CSPs was carried in blow-through sampling bomb in nitrogen at different pressures [14]. We used the CSP 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 CSPs 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 CSP 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.

3. Results and discussion

3.1. Ignition characteristics of CSPs

The values of the time of gasification and ignition, recoil force of gasification products outflow for the solid propellants samples under study in atmospheric conditions were determined with use of laser set-up, Fig. 1. Processing of signal recording from the recoil force transducer we get the time delays of gasification t_{gas} and ignition t_{ign},, the value of the recoil force F outflow of gasification products from the burning surface of CSP samples. Examples of records are shown in Fig. 2. The ignition time of CSPs versus the maximum value the heat flux density (in the center of the laser beam) dependences were determined, see in Fig. 3.

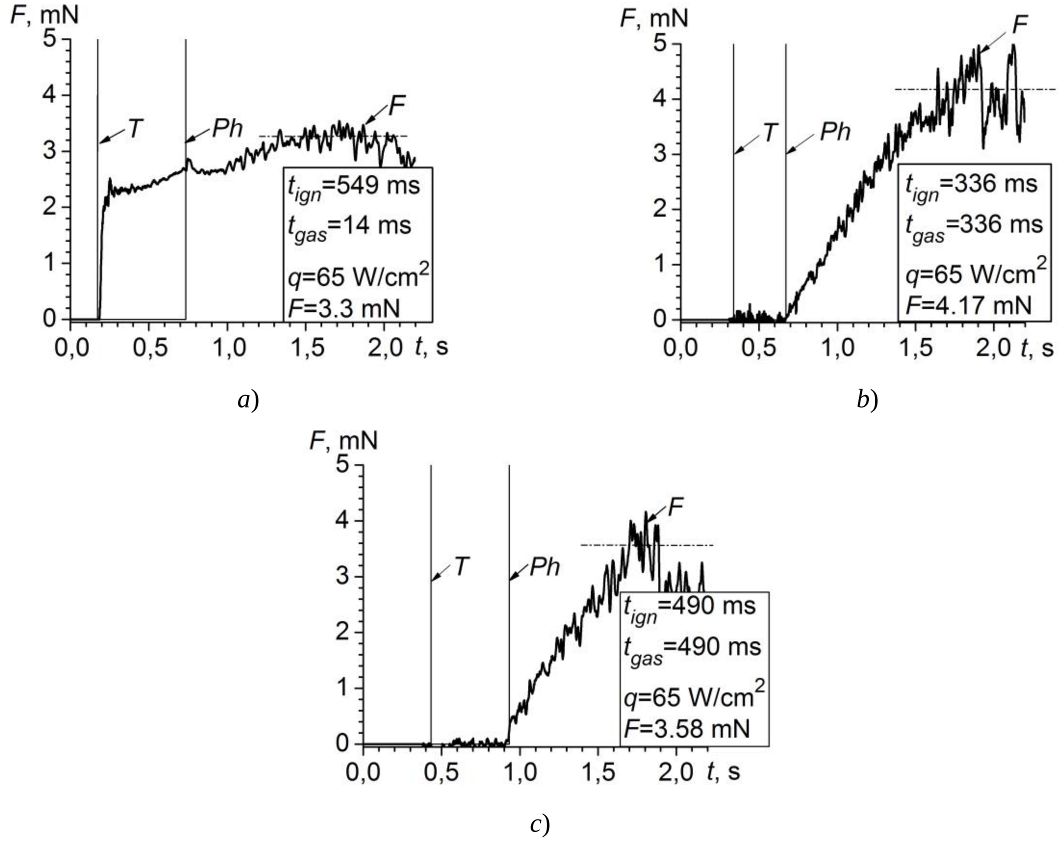

Figure 2: The signals of thermocouple (*T*), photodiode (*Ph*) and the recoil force transducer (*F*) that have been recorded at q_{max} = 65 W/cm^2 over time interval embracing the heating, ignition and combustion processes for CSPs with Alex (*a*), Alex+Fe (*b*) and Alex+B (*c*)

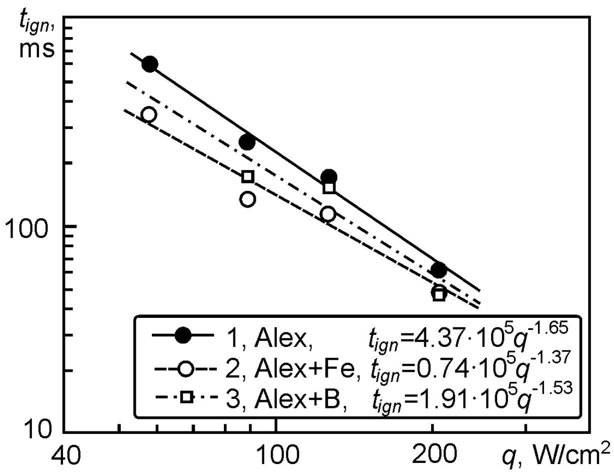

Figure 3: The ignition time of CSPs from the heat flux density

Partial replacement of Alex by iron UFP in CSP leads to the decrease of the ignition time 1.3–1.9 times in the range of heat flux density 55–220 W/cm^2. Partial replacement of Alex by boron UFP in CSP leads to the decrease of the ignition time 1.2–1.4 times in the specified range of *q*. For CSP sample with Alex the gasification start immediately after the shutter opens and the gasification time delay 40 times less than the ignition time at the heat radiant flux density of $q_{max} = 65$ W/cm^2. For samples with Alex+Fe and Alex+B the time moments of ignition start and gasification start coincides. Partial replacement of Alex by iron UFP in CSP at the initiation a CO_2-laser leads to the increase the gasification time 25 times and the increase of the recoil force of gasification products outflow from burning surface 1.3 times in the period of stationary combustion of CSPs. For the partial replacement of Alex by boron UFP in the CSP composition the gasification time increases 36 times and the recoil force of gasification products outflow increases 1.1 times. Thus, the additives of iron and boron UFPs in the aluminized CSPs allows to considerably increase the gasification time and reduce the ignition time and also increase the recoil force of gasification products outflow from the burning surface of CSP samples.

3.2. Combustion characteristics of CSPs

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

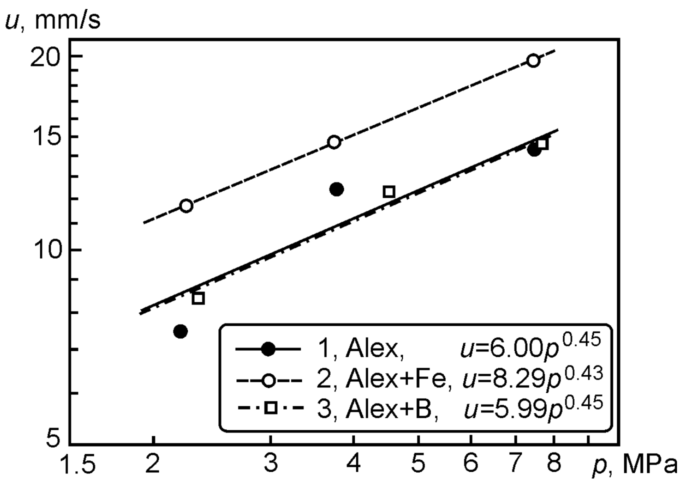

Figure 4: The burning rate of CSPs from pressure

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

CSP sample	***u*, mm/s**	m_{ccp}
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 CSP 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 CSPs practically does not change at nitrogen pressure ~ 4 MPa.

For partial replacement of Alex by boron UFP in CSP the burning rate and relative mass of CCPs at pressure ~ 4 MPa are virtually unchanged. The burning rates of CSPs 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 CSPs burning rate correlates well with the data of recoil force of gasification products outflow from burning surface of samples (see Fig. 2).

3.3. Particle size and phase 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 Fig. 5.

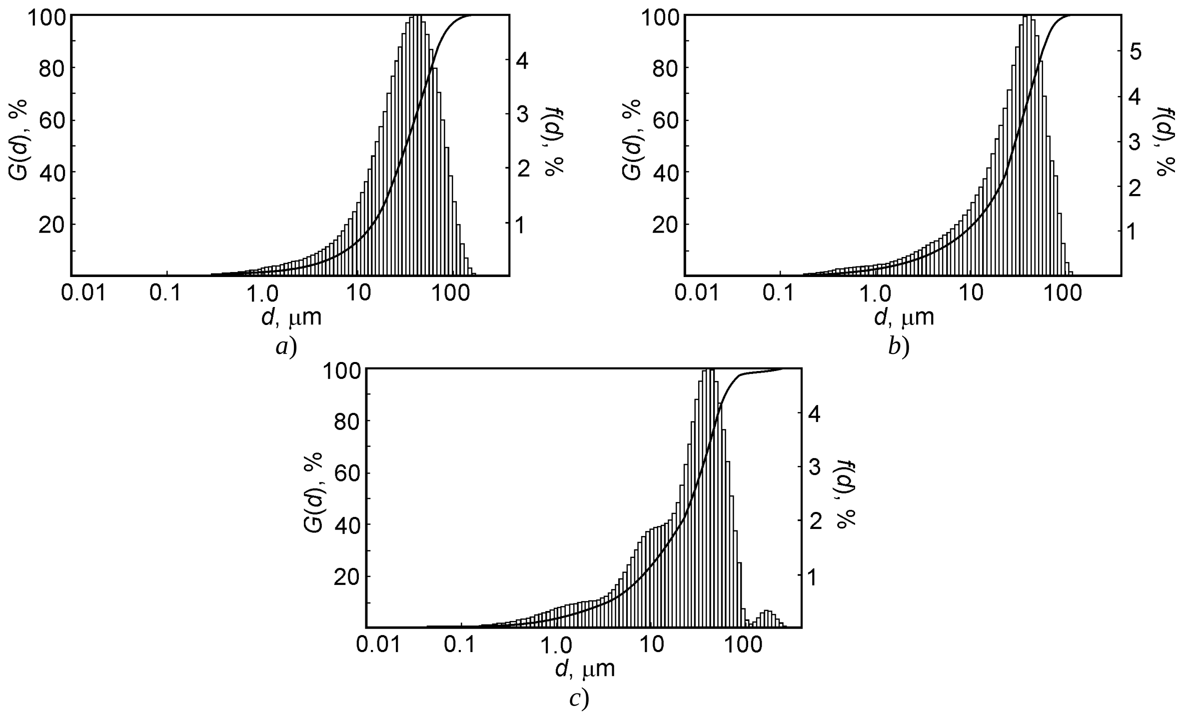

Figure 5: Differential and cumulative mass size distribution function of CCP particles with Alex (*a*), Alex+Fe (*b*) and Alex+B (*c*)

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 CSPs 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 CSP composition decreases the mean particle diameter d_{43} from 37.4 to 33.5 μm. Partial replacement of Alex by boron UFP in CSP 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

CSP 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 CSP 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 CSP, 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 CSP sample.
Partial replacement of Alex by boron UFP in CSP 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

1. The effects of additives of iron and amorphous boron UFPs in composite solid propellants on the basis of AP, butadiene rubber and 15.7 wt. % of aluminum Alex UFP on the ignition and combustion characteristics were studied. The ignition was performed with CO_2-laser in air at atmospheric pressure. 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.
2. It was found that partial replacement of Alex by 2 wt. % iron UFP in CSP decreases the ignition time by 1.3–1.9 times at the range of heat flux density 55–220 W/cm^2, the increase of the recoil force of gasification products outflow from burning surface 1.3 times in the period of stationary combustion of samples, the increase of the burning rate 1.3–1.4 times at the range of nitrogen pressure 2.0–7.5 MPa and reduction of the mean diameter of CCP particles d_{43} 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 increases 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 CSP, 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.
3. Partial replacement of Alex by boron UFP in CSP decreases the ignition time 1.2–1.4 times at q = 55–220 W/cm^2 and the increase of the recoil force of gasification products outflow from the burning surface 1.1 times. In this the burning rate of CSP does not change at the range of pressure 2.0–7.5 MPa, the mean diameter of CCPs particles d_{43} 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.

Acknowledgement

This work was partially supported by the Russian Foundation for Basic Research (project No. 15-33-50066 «Research of ignition and combustion processes of high-energy nanocomposites based on ammonium nitrate» and project No. 15-03-04321 «Ignition and combustion of metal fuel particles based on aluminum and boron»), carried out in 2015 was supported by «The Tomsk State University Academic D.I. Mendeleev Fund Program» grant No 8.2.46.2015, was financially supported from the Ministry of Education and Science of the Russian Federation within the framework of the Federal Target Program Agreement No. № 14.578.21.0034 (RFMEFI57814X0034)

References

[1] Beckstead, M.W., Puduppakkama, K., Thakreb, P., and Yang, V. 2007. Modeling of combustion and ignition of solid-propellant ingredients. *Progress in Energy and Combustion Science* 33:497–551.

[2] Takahashi, K., Oide, Sh., and Kuwahara, T. 2013. Agglomeration characteristics of aluminum particles in AP/AN composite propellants. *Propellants, Explosives, Pyrotechnics* 38:555–562.

[3] Sossi, A., Duranti, E., Manzoni, M., Paravan, C., DeLuca, L.T., Vorozhtsov, A.B., Lerner, M.I., Rodkevich, N.G., Gromov, A.A., and Savin, E.N. 2013. Combustion of HTPB-based solid fuels loaded with coated nanoaluminum. *Combustion Science and Technology* 185:17–36.

[4] Arkhipov, V.A., and Korotkikh, A.G. 2012. The influence of aluminum powder dispersity on composite solid propellants ignitability by laser radiation. *Combustion and Flame* 159:409–415.

[5] Arkhipov, V.A., Bondarchuk, S.S., Korotkikh, A.G., Kuznetsov, V.T., Gromov, A.A., Volkov, S.A., and Revyagin, L.N. 2012. Influence of aluminum particle size on ignition and nonstationary combustion of heterogeneous condensed systems. *Combustion, Explosion, and Shock Waves* 48:625–635.

[6] Arkhipov, V.A., Bondarchuk, S.S., and Korotkikh, A.G. 2010. Comparative analysis of methods for measuring the transient burning rate. II. Research results. *Combustion, Explosion, and Shock Waves* 46:570–577.

[7] Shioya, S., Kohga, M., and Naya, T. 2014. Burning characteristics of ammonium perchlorate-based composite propellant supplemented with diatomaceous earth. *Combustion and Flame* 161:620–630.

[8] Ishitha, K., and Ramakrishna, P.A. 2014. Studies on the role of iron oxide and copper chromite in solid propellant combustion. *Combustion and Flame* 161:2717–2728.

[9] Farley, C.W., Pantoya, M.L., and Levitas, V.I. 2014. A mechanistic perspective of atmospheric oxygen sensitivity on composite energetic material reactions. *Combustion and Flame* 161:1131–1134.

[10] Berner, M.K., Talawar, M.B., and Zarko, V.E. 2013. Nanoparticles of energetic materials: synthesis and properties (Review). *Combustion, Explosion, and Shock Waves* 49:625–647.

[11] McDonald, B.A., Rice, J.R., and Kirkham, M.W. 2014. Humidity induced burning rate degradation of an iron oxide catalyzed ammonium perchlorate/HTPB composite propellant. *Combustion and Flame* 161:363–369.

[12] Zarko, V.E., and Glotov, O.G. 2013. Formation of Al oxide particles in combustion of aluminized condensed systems (Review). *Science and Technology of Energetic Materials* 74:139–143.

[13] Arkhipov, V.A., Kiskin, A.B., Zarko, V.E., and Korotkikh, A.G. 2014. Laboratory method for measurement of the specific impulse of solid propellants. *Combustion, Explosion, and Shock Waves* 50:622–624.

[14] Glotov, O.G., and Zyryanov, V.Ya. 1995. Condensed combustion products of aluminized propellants. I. A technique for investigating the evolution of disperse-phase particles. *Combustion, Explosion and Shock Waves* 31:72–78.