CONDENSED COMBUSTION PRODUCTS OF SOLID PROPELLANT WITH BORON ADDITIVE

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Abstract

The sampling method was used to investigate the condensed combustion products of two model propellants. Basic formulation contained 64.6 % of bidisperse AP, 15.7 % of Alex (Russian aluminum nanopowder obtained by the electric explosion in argon of Al wire) and 19.7 % of binder (butadiene rubber plasticized with transformer oil). In another formulation 2 % of Alex was replaced by boron. The experiments were performed at three pressure levels, ca. 2.2 MPa, 4.5 MPa and 7.5 MPa. The data on particle size, morphology and combustion completeness are presented as well as the burning rate law in the pressure range 2.2-7.5 MPa. The boron additive has no effect on burning rate law but intensifies the agglomeration via increasing the agglomerate mass and size.

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Introduction

The potential of using traditional powder aluminum as metal fuel in the composite solid propellants is really limited. Therefore numerous attempts to improve the burning characteristics of aluminum connected with its behavior in a combustion wave, for example, to facilitate the ignition, to reduce the agglomeration, to increase the combustion completeness, etc. are made. One of the possible ways of modification of aluminum fuel – increase of its dispersion by partial or full replacement by so-called nanoAl, in particular, by Alex – the powder produced via electric explosion of wires. The properties of nanoAl and their effect on the burning parameters of propellant compositions are investigated in many works, of for example [1-7]. Alternative ways of modification of metal fuel are: a metal doping (introduction of additives into the volume of particle); a covering of a surface of particles; introduction of additional fuel, catalytic or other active component in a propellant formulation. The specified ways make effect on properties of metal particle and its oxide shell, affect physical and chemical processes of interaction between the particles and between the particles and reagents released by other components of composite system. Listed properties and processes determine the ignition, oxidation, agglomeration of particles of metal fuel in the reaction zone of the condensed phase. In works [8, 9] the propellants with mechanical alloys of Al and B are investigated. In comparison with aluminum, boron has higher caloric value, ignites at lower temperature, and forms (under certain conditions) smaller amount of the condensed combustion products [10]. It makes the boron attractive as additional fuel in combination with aluminum. It should be noted that the attempts described in literature of getting better behavior of aluminum did not lead to outstanding results, though they showed often the encouraging tendencies [8, 9]. In this work we investigate the effects of full replacement of traditional aluminum by Alex and introduction of a boron additive. The goal of work is obtaining information on the burning rate law and on the condensed combustion products for the basic (with Alex) and for modified (with Alex+B) model solid propellants.

Propellants and specimens, experimental technique and conditions

Two composite propellants consisting of 64.6% (hereinafter mass %) of bidisperse AP (fractions less than 50 microns and 160–315 micron in the ratio 40/60); 19.7% of binder based on butadiene rubber plasticized by transformer oil; and 15.7% of metal fuel are investigated. In the first - basic - formulation all 15.7% of fuel is the ultra-fine aluminum powder, Alex. The fuel in the second formulation consists of 13.7% of Alex and 2% of amorphous boron.

Specific surface area is 7.04 m^2/g for Alex and 8.63 m^2/g for boron. Measurements were performed using the Nova 2200e analyzer in nitrogen by BET method.

Specimens for the combustion tests had a form of the cylinder with a diameter of 10 mm, and high about 30 mm. They were made by extrusion pressing with the subsequent curing. The mass of a sample was about 4 g, the density of samples was in an interval of 1.56-1.59 g/cm^3. The lateral surface of samples was covered with inhibiting layer made of heat-resistant rubber Solprene®.

Size analysis for particle fraction <80 microns was performed using an automatic granulometer Malvern 3600E. Other fractions were analyzed by the optical microscopy method. The chemical analysis of particles was carried out by a permanganatometric method [2] to determine the metallic (unburned) aluminum content. The fractions were analyzed whenever possible separately, but in the case of small mass the fractions were united in one probe.

Experiments are made at three pressure levels, ca. 2.2 MPa, 4.5 MPa and 7.5 MPa with use of sampling technique [11]. Application of the burning-out material for inhibiting layer allowed to extinguish the particles near a specimen burning surface. A distance for particle moving before extinguishment can be estimated as 30 mm. The burning rate was calculated using the known length of a specimen and the burning time, derived from the pressure-versus-time record. The sampled particles of the condensed combustion products (CCP) were divided onto 4 fractions: < 80 micron, 80-160 micron, 160-315 micron and > 315 micron. They were then subjected to morphological, particle size and chemical analyses. Size analysis for particles < 80 micron fraction, was performed using automatic granulometer Malvern 3600E sizer. Other fractions were analyzed by optical microscopy method. The chemical analysis of particles was carried out by a permanganatometric method [2] allowing one to determine the amount of the unburned aluminum.

Representation of the results and determination of parameters

Results of the particle size and the chemical analysis are represented in the form of histograms of the density of the sizes distribution of the

relative mass of CCP $f_i(D) = m_i /(M_{prop} \cdot \Delta D_i)$,

and the relative mass of aluminum in CCP $f_i^{Al}(D)= f_i(D) \cdot \varepsilon_j^{Al}$,

where m_i – the mass of CCP in *i*-th a histogram size interval, ΔD_i – width of this size interval, ε_j^{Al} – the mass content of unburned aluminum in *j*-th CCP fraction to which *i*-th histogram size interval belongs. Further the index *i* is omitted, the functions *f(D)* and $f^{Al}(D)$ shortly called as "mass distributions".

As a rule, *f(D)* and $f^{Al}(D)$ function graphs have the expressed local minimum (designated as D_L) that allows one to consider and analyze separately the coarse particles-agglomerates with $D > D_L$ and the fine oxide particles with $D < D_L$ [12]. For propellants under study D_L = 55 micron that corresponds to the rounded value of the right border of the 15th size interval of the Malvern 3600E sizer. With use of *f(D)* and $f^{Al}(D)$ functions we calculate the mean sizes (diameters) D_{mn}, and also a set of dimensionless mass parameters. Scaling was made via division by the propellant mass. For example, $m_f = M_f /M_{prop}$ is the dimensionless mass of fine particles, where M_f and M_{prop} are the mass of fine particles and propellant specimen mass in grams.

In this work we used the following parameters: m_f - mass of fine particles, m^{Al}_f – mass of unburned aluminum in fine particles, m_{ag} – mass of agglomerates, m^{Al}_{ag} – mass of unburned aluminum in agglomerates, $m_{ccp} = m_f + m_{ag}$ – total mass of CCP, $m^{Al}_{ccp} = m^{Al}_f + m^{Al}_{ag}$ – total mass of unburned aluminum in CCP, m_{ag}/m_{ccp} – mass fraction of agglomerates in CCP, $m^{Al}_{prop} \equiv 0.157$ – initial mass of aluminum in propellant, $\eta = m^{Al}_{ccp}/m^{Al}_{prop}$ – incompleteness of aluminum combustion, i. e., total relative quantity of unburned aluminum in CCP.

It should be noted that the values of parameters presented below which were calculated with use of the permanganatometric data on the unburned aluminum content, are approximate. In calculation of the combustion incompleteness η we assumed $m^{Al}_{prop} = 0.157$. As a first approximation we consider that the metal fuel in both compositions is 100%-pure aluminum, and also we assume that the boron behaves similar to aluminum in permanganatometric analycal procedure. At the same time it is known that the content of metal aluminum in Alex powders can be significantly lower (for example, about 85% [2]). For obtaining more précised data on combustion completeness with combined metal fuel Al+B it should be used a special method of chemical analysis, for example, cerimetric one [13].

Experimental results and discussion

Table 1 presents the data on dependencies of burning rate on pressure. The determination coefficient R^2 characterizes quality of approximation.

Table 1:

Parameters of the burning rate law in form $r = Bp^n$, where r in [mm/s], p in [MPa]

Propellant with fuel	B	n	R^2
Alex	6.00±1.99	0.45±0.20	0.70
Alex+B	5.99±0.66	0.45±0.08	0.95

Table 2 presents the chemical analysis data on the unburned aluminum content in different fraction of CCP.

Table 2: Percentage of metal aluminum in the separate fractions of CCP and averaged over all fractions value (%$\mathrm{Al}_{\mathrm{av}}$) at pressure variation

Fuel	p, MPa	%$\mathrm{Al}_{\mathrm{av}}$	In table cells – %Al in fractions			
			<80 µm	80-160 µm	160-315 µm	> 315 µm
Alex	2.2	1.64	0.65 ± 0.03	15.3 ± 0.1		
Alex	3.8	1.21	0.41 ± 0.01	8.1 ± 0.7		
Alex	7.5	0.98	0.67 ± 0.09*	4.50 ± 0.05		
Alex+B	2.3	2.62	1.29 ± 0.05	5.5 ± 0.2*	5.0 ± 0.1	
Alex+B	4.5	1.81	0.87 ± 0.03	3.65 ± 0.05*	3.54 ± 0.06	
Alex+B	7.7	1.56	0.83 ± 0.01	3.1 ± 0.2	3.35 ± 0.05	

Comments:

1) The cells joining means merging of the relevant fractions before the analysis. The absence of a cell means absence of particles of the relevant fraction.

2) In all cases, except marked with a sign (*), average results of two independent determinations are presented. In the cases marked (*), the number of independent analyses was n = 3. The figure after sign ± is a mean square deviation.

Apparently, in all cases the Al content in fraction <80 micron do not exceed 1.3%. It is expected that in smaller particles (less than 55 micron in size) the quantity of not oxidized aluminum is even less. Therefore the particles with size less than 55 micron can be apparently considered as oxide particles. It should be noted that for the propellants under study the metal aluminum content in agglomerates (i. e. in fractions > 80 micron, see table 2) is relatively small (≈ 3% … 15%).

The fragments of mass distributions of CCP corresponding to the agglomerate particles are shown in figure 1. Values of characteristic parameters are given in table 3, figure 2 serves for their comparison. Columns and points of plots in figure 2 correspond to the pressure levels written under graphs. The general height of a column corresponds to m_{ccp} value, that is total relative mass of CCP. The dark color column allocated inside m_{ccp}-column is m_{ag} – the relative mass of agglomerates. Points with line-segments graphs show dependencies of the agglomerate size on pressure.

Analyzing table 3 and figure 1, 2 data, we note the following:

● Masses of CCP for both propellants with Alex and Alex+B are close in size. In case of propellant with Alex for all pressures studied the mass of CCP is higher, but the difference only slightly exceeds the confidential interval. The CCP-mass almost does not change under pressure variation (cf. height of columns and intervals of an error at columns in figure 2 for both propellants), any noticeable tendency is absent.

● Mass of agglomerates m_{ag} (dark columns in figure 2) for both propellants exhibits an unexpected tendency of growth with pressure. One can assert that in the case of propellant with Alex+B the mass of agglomerates m_{ag}, the portion of agglomerates in CCP m_{ag}/m_{ccp} and agglomerate mean diameter D_{43}, are much larger.

In view of the close levels of burning rate, and also identity of geometrical structure of propellants (that mainly is defined by AP particles), the listed facts can be treated as intensification of agglomeration at boron introduction.

● Mass-size distribution functions of agglomerates (figure 1) for propellants with Alex and with Alex+B have a number of differences. Despite a comparable amplitude of a maximum, the area under the function plot in case of propellant with Alex+B is larger. For all pressure levels the mass distribution function of agglomerates in case of propellant with Alex+B has greater width and longer right tail, and its maximum is located more far to the right.

Feature of mass distributions of agglomerates of propellant with Alex – existence of mode located around 100 micron which, in particular, supplies with mass the range the left of mode (in figure 1 in the size range of 55-100 micron). These particles and their mass can be associated with the burning out of agglomerates. According to tables 2, 3 data, at increase in pressure 2.2 MPa → 3.8 MPa → 7.5 MPa, incompleteness of combustion of η changes in sequence 0.033 → 0.023 → 0.020; the percentage of metal aluminum in particles of 80-315 micron decreases as ≈ 15% → ≈ 8% → ≈ 5%. However, the mean diameter D_{43} changes only slightly: 108 micron → 119 micron → 117 micron at an instrumental error ± 9 micron.

Transformation of mass distribution in the process of burning out of aluminum is caused by numerous factors that act "in opposite directions". It is known [15] that small size particles burn out (consume metal aluminum) faster, than the large ones. It is known [16] that the portion of the oxide accumulated on the surface of the burning particle in the form of cap increases with the diameter of a particle. For propellant with Alex+B the burning out of agglomerates results in redistribution of CCP mass into interval of 55-100 micron. At increase in pressure in sequence 2.3 MPa → 4.5 MPa → 7.7 MPa, the combustion incompleteness η changes in sequence 0.047 → 0.034 → 0.029; the percentage of metal aluminum in particles of 80-315 micron decreases as ≈ 5% → 4% → 3%. The mean diameter D_{43} changes as follows: 177 micron → 203 micron → 195 micron. The incompleteness of aluminum combustion η in the case of propellant with Alex+B is twice higher than that for propellant with Alex, see table 3. Nevertheless unburned metal is "gathered" due to bigger agglomerates mass in spite of the fact that metal content in the Alex+B agglomerates is lower, than that in the case of the propellant with Alex (table 2). Burning rate and geometrical structure for propellants with Alex and Alex+B are comparable. Thus, the thickness of preheated and reaction zones are also comparable. However, the propellant with Alex+B, in comparison with propellant with Alex, forms the bigger mass of sizable agglomerates which, nevertheless, are characterized by more complete burning out of aluminum. The reasons of observed regularities, obviously, are specific features of agglomeration process. One may assume that the presence of boron leads to more active reaction in the condensed phase, but hinders the agglomerate detachment.

The analysis of mass distributions of oxide particles smaller than 55 micron in size showed the following:

- In all cases the main modes of mass distributions are located in the same intervals of the Malvern sizer. So, the first mode is observed in the range of 1.9–2.4 micron. In the case of Alex+B propellant its amplitude is 2.5-4 times higher, than in the case of propellant with Alex. Formation of particles of the micron and sub-micron size is related usually with the vapor-phase combustion of aluminum [12, 17].
- The size distributions demonstrate the trend to shift the modes to the right when pressure increases, for example (6.4–8.2 micron → 13.6–17.7 micron); (13.6–17.7 micron → 17.7–23.7 micron), or emergence of modes in the specified intervals. Formation of oxide particles of the corresponding sizes can be associated with the complete burn-out of non-agglomerating aluminum particles and of agglomerates of small sizes (< 100 micron). Corresponding oxide particles are formed as a result of constringency to the sphere of an oxide cap after total metal consumption.
- In the case of propellant with Alex more expressed filling of the size interval 33.7-55 micron takes place. Presumably, the complete burning out of aluminum from agglomerates of the modal size about 100 micron is responsible for appearance of particles with the sizes of 30-70 micron. These particles are also formed through the mechanism of spheroidizing an oxide cap. In the case of fuel Alex+B the effect of populating the interval of 33.7-55 micron is less expressed and it is noticeable only in the case of pressure 7.7 MPa. Apparently, it is because the agglomerates aluminum burning out process is mostly finished before their detachment, i. e. within the condensed phase.

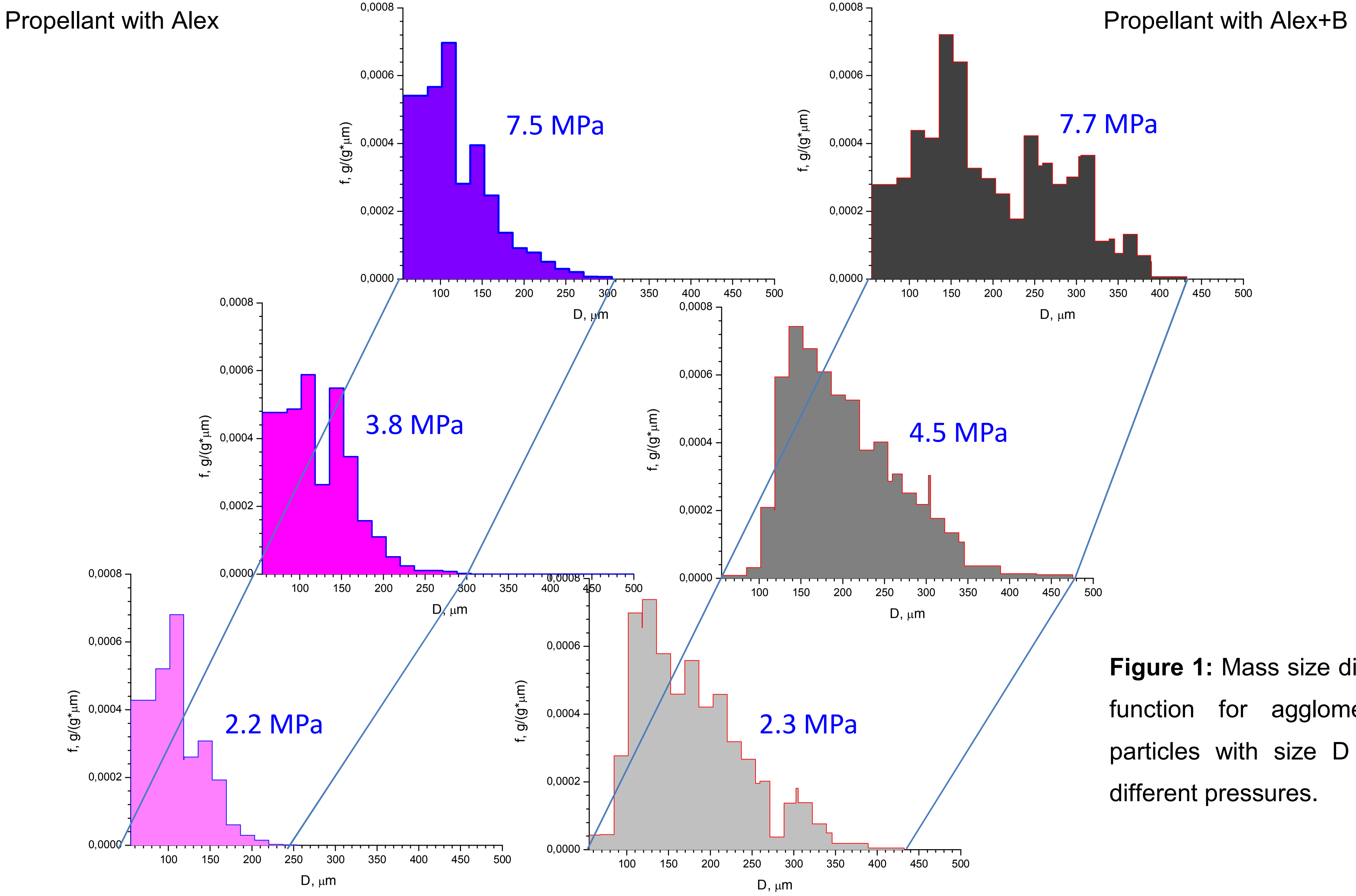

Figure 1: Mass size distribution function for agglomerates – particles with size $D > D_L$ at different pressures.

Table 3: Pressure *p*, burning rate *r* and CCP characteristic parameters

Fuel	*p*, MPa	*r*, mm/s	m_{ccp}	m^{Al}_{ccp}	η	m_f	m^{Al}_f	m_{ag}	m^{Al}_{ag}	m_{ag}/m_{ccp}	d_{30}, μm	D_{43}, μm
Alex	2.2	7.5	0.3116	0.0051	0.0326	0.2639	0.0018	0,0477	0,0033	0.1532	6.4	108
Alex	3.8	12.4	0.3017	0.0037	0.0233	0.2400	0.0010	0.0582	0.0024	0.1929	6.7	119
Alex	7.5	14.3	0.3168	0.0031	0.0198	0.2567	0.0017	0.0601	0.0014	0.1897	6.2	117
Alex+B	2.3	8.4	0.2791	0.0073	0.0466	0.1854	0.0025	0.0937	0.0048	0.3357	4.8	177
Alex+B	4.5	12.3	0.2949	0.0053	0.0341	0.1928	0.0017	0.1020	0.0036	0.3459	6.5	203
Alex+B	7.7	14.6	0.2930	0.0046	0.0292	0.1881	0.0016	0.1050	0.0030	0.3584	4.8	195

Comments:

Here d_{30} and D_{43} – mean diameters for oxide particles and for agglomerates. They are calculated using *f(D)* functions in corresponding size ranges. The relative error of the d_{30} size reported by the producer of Malvern 3600E amounts ±4 %. The absolute error of the D_{43} amounts ≈ ±9 micron.

The calculated mass parameters are specified with four digits after a decimal point in order to avoid misunderstanding because of rounding of small values. The confidential interval for these parameters does not exceed ±15 relative % and typically is about ±10 relative % at the significance level of 68% [14].

In experiments with the Alex-containing propellant at 3.8 MPa, $m_{ccp} > m_{ag} + m_f$ and $m^{Al}_{ccp} > m^{Al}_{ag} + m^{Al}_f$. In this case in CCP there are large irregular agglomerates, often non-spherical form. Such agglomerates probably are formed by accumulation of metal on inhibiting layer. They were excluded from consideration at calculations of m_{ag}, m^{Al}_{ag}, m_{ag}/m_{ccp}, D_{43}. However, the metal aluminum containing in these particles taken into account in calculation of m^{Al}_{ccp} and η.

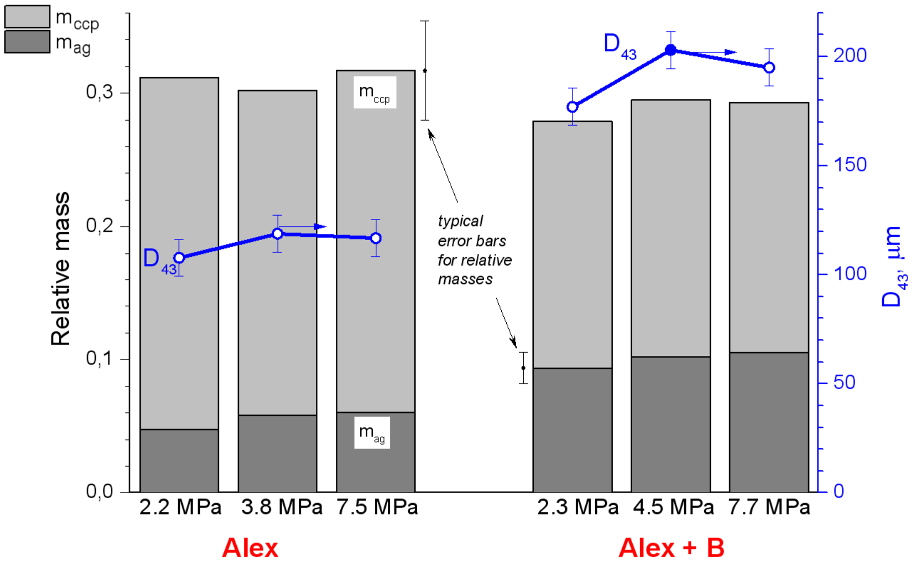

Figure 2: Comparison of the dimensionless mass parameters m_{ccp} and m_{ag} and mean sizes D_{43} for agglomerates which are formed when firing the propellants with Alex and Alex+B at different pressures.

Conclusions

Results of this experimental study showed that the replacement of 2% from 15.7% of metal fuel Alex by amorphous boron in the formulation with AP and the butadiene rubber based binder plasticized with transformer oil, slightly influences the burning rate law, but manifests in changing the characteristics of agglomeration and the condensed combustion products sampled at pressure about 2.2, 4 and 7.5 MPa when particles are extinguished at 30 mm distance from a specimen. Propellant with Alex+B, in comparison with propellant with Alex, is characterized by the relatively bigger mass of agglomerates, a bigger portion of agglomerates among the condensed combustion products, larger sizes of agglomerates, and higher total incompleteness of combustion of aluminum. At the same time, the material of the sampled agglomerates is characterized by low percentage (3.5–5%) of unburned aluminum. Presumably, presence of boron promotes the oxidizing reaction of metal fuel in the condensed phase, but hinders the agglomerate detachment that leads to growth of their sizes and masses. The results received do not reject entirely the possibility of achievement of a positive effect from use of the combined metal fuel based on Al and B. It seems to be of interest to investigate in future the potential of introducing of a small additive of aluminum to boron for its "activation".

References

[1] GLOTOV O. G., ZARKO V. E., BECKSTEAD M. W. Agglomerate and oxide particles generated in Combustion of Alex containing solid propellants / Energetic Materials. Analysis, diagnostics and testing. 31st Int. Annual Conf. of ICT, Karlsruhe, Germany. **2000**, p. 130-1-130-14.

[2] FEDOTOVA T. D., GLOTOV O. G., ZARKO V. E. Chemical Analysis of Aluminum as a Propellant Ingredient and Determination of Aluminum and Aluminum Nitride in Condensed Combustion Products // Propellants, Explosives, Pyrotechnics. **2000**, V. 25, No. 6, p. 325-332.

[3] ZARKO V. E., GLOTOV O. G., SIMONENKO V. N., et al. Study of the combustion behavior of solid propellants containing ultra fine aluminum // CD Proc. of Int. Conf. on Combustion and Detonation. Zel'dovich Memorial II. Moscow **2004**, Report WS1-6, 37 p.

[4] DELUCA L. T., GALFETTI L., SEVERINI F., et al Burning of Nano-Aluminized Composite Rocket Propellants // Combustion, Explosion, and Shock Waves. **2005**, V. 41, No. 6, p. 680-692.

[5] ARKHIPOV V. A., BONDARCHUK S. S., KOROTKIKH A. G., et al. Influence of aluminum particle size on ignition and nonstationary combustion of heterogeneous condensed systems // Comb., Explos, & Shock Waves. **2012**, V. 48, No. 5, p. 625–635.

[6] FEDOROV S. G., GUSEINOV S. L., STOROZHENKO P. A. Nanodispersed metal powders in high-energy condensed systems // Nanotechnologies in Russia, **2010**, V. 5, No. 9-10, p. 565-582.

[7] JAYARAMAN K., CHAKRAVARTHY S. R., SARATHI R. Accumulation of nano-aluminium during combustion of composite solid propellant mixtures // Combustion, Explosion, and Shock Waves. 2010, V. 46, No. 1, p. 21-29.

[8] GLOTOV O. G., SIMONENKO V. N., ZARKO V. E., et al. Combustion characteristics of propellants containing aluminum-boron mechanical alloy / Energetic materials. Structure and properties. 35th Int. Ann. Conf. of ICT, Karlsruhe, Germany, **2004**, p. 107-1–107-18.

[9] GLOTOV O. G., ZARKO V. E., SIMONENKO V. N., et al. Effect of Al/B mechanical alloy on combustion characteristics of AP/HMX/energetic binder propellants / Energetic Materials. Performance and Safety. 36th Int. Ann. Conf. of ICT & 32nd Int. Pyrotech. Seminar, Karlsruhe, Germany. **2005**, p. 102-1–102-12.

[10] Combustion of Boron-Based Solid Propellants and Solid Fuels / K. K. Kuo, R. Pein (Eds.), CRC Press, Boca Raton, **1993**.

[11] GLOTOV O. G., ZYRYANOV V. YA. Condensed combustion products of aluminized propellants. I. A technique for investigating the evolution of disperse-phase particles // Combustion, Explosion and Shock Waves. **1995**, V. 31, No. 1, p. 72–78.

[12] ZARKO V. E., GLOTOV O. G. Formation of Al oxide particles in combustion of aluminized condensed systems (Review) // Sci. Tech. Energetic Materials. **2013**, V. 74, No. 6, p. 139–143.

[13] FEDOTOVA T. D., GLOTOV O. G., ZARKO V. E. Application of Cerimetric Methods for Determining the Metallic Aluminum Content in Ultrafine Aluminum Powders // Propellants, Explosives, Pyrotechnics. **2007**, V. 32, No. 2, p. 160–164.

[14] GLOTOV O. G. Condensed Combustion Products of Aluminized Propellants. IV. Effect of the Nature of Nitramines on Aluminum Agglomeration and Combustion Efficiency // Combustion, Explosion, and Shock Waves. **2006**, V. 42, No. 4, p. 436–449.

[15] GLOTOV O G, ZARKO V E, KARASEV V V, et al. Macrokinetics of Combustion of Monodisperse Agglomerates in the Flame of a Model Solid Propellant // Combustion, Explosion, and Shock Waves. **2003**, V. 39, No. 5, p. 552–562.

[16] GLOTOV O. G., ZHUKOV V. A. The Evolution of 100-μm Aluminum Agglomerates and Initially Continuous Aluminum Particles in the Flame of a Model Solid Propellant. II. Results // Combustion, Explosion, and Shock Waves, **2008**. V. 44, No. 6, p. 671–680.

[17] GLOTOV O. G. Condensed Combustion Products of Aluminized Propellants. III. Effect of an Inert Gaseous Combustion Environment // Combustion, Explosion, and Shock Waves, **2002,** V. 38, No. 1, p. 92–100.