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Agglomeration and combustion completeness of boron in composite propellant

Glotov Oleg, Zarko Vladimir, Surodin Grigory and Kiskin Alexander
Voevodsky Institute of Chemical Kinetics and Combustion
Siberian Branch of the Russian Academy of Sciences (ICKC SB RAS)
Institutskaya street, 3, Novosibirsk 630090, Russia. Corresponding author: glotov@kinetics.nsc.ru

Abstract

The object under study is the composite model propellant based on ammonium perchlorate, energetic binder, and boron. The goal of the work is to experimentally investigate the effect of propellant formulation on boron combustion efficiency in composite propellants. The first study stage involved variations in boron content (12%...40%). The second stage was focused on the complete substitution of boron by either aluminum diboride or mechanical aluminum-boron mixture. Experiments were performed in nitrogen at pressures of 1.2 MPa and 2.5 MPa. The data are presented on the burning rate; morphological, granulometric, and chemical composition of particles quenched near a burning surface.

1. Introduction

Boron is characterized by an extremely high calorific value, but the amount of oxygen spent for its oxidation is about 2.5 times larger than that for aluminum [1]. Therefore, boron is considered mainly as a candidate for air-breathing propulsion systems [2–6]. Promising are the fuel-rich propellants containing up to 55 mass % of boron [6]. However, the boron usage has a disadvantage. It is difficult to burn up boron with a high conversion efficiency. Thus, one must "activate" boron combustion and find some specific design solutions [4–6]. The well-known way of boron activation is the usage of boron compounds (borides, carbide B_4C), boron alloys, and also coatings, non-traditional oxidizers [7]. In particular, the idea to use aluminum boride as a solid propellant component was proposed in the 1970s [6]. Despite thorough studies and numerous reports on ramjets and on boron combustion [1–8], the problem of increasing the combustion efficiency of boron-containing propellants is still open for discussion. Thus, noteworthy is to mention the following. Since the boron has the high calorific value, its partial substitution often leads to a decrease in the "energetic capacity" of metallic fuels and propellants. Therefore, firstly one has to solve the optimization problem, i. e., how much boron one can spend for increase the combustion efficiency of the remaining part of fuel. Secondly, the ramjet should be designed as a joint system propellant+motor, because the conditions for propellant combustion are determined by many factors, which depend on concrete, technical solutions. Thus, there is no unique criterion for choosing the optimal propellant, and in experiments the burning conditions should simulate closely the full-scale ones.

At the same time, there is need for basic information on the combustion of boron and boron-containing fuels in propellants without reference to any engine. Of particular interest are the parameters of particles ejecting from the burning surface because they determine the initial conditions for particle's evolution upon movement inside the motor. For instance, the primary combustion products characteristics for propellant (33% B, 5% Mg, 27.5% AP 29.5% HTPB) are discussed in [9]. However, the data on boron agglomeration are scarce [10], and no systematic comparison is performed of the combustion characteristics of the propellants, realized for one or another modification of the boron-containing fuel. There are the works focused on obtaining given burning rate by varying propellant composition [11], but there are no works on the optimization of metallic fuel combustion by obtaining necessary parameters for the particles leaving the propellant.

The goal of this work is to get novel knowledge about the influence of formulation and pressure on the burning rate and on the combustion efficiency of boron-containing fuels. To this end, the original sampling method was used to study particle characteristics (morphology, granulometric and chemical composition).

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2. Components, formulations, and propellant specimens. Experimental program and technique

Below listed are the components used to produce model propellants (Table 1). Binder is the active fuel binder based on methylpolyvinyl-tetrazole polymer plasticized by nitro compounds [12]. «Metallic» fuels: B – amorphous boron ~ 3 micron, Al – ASD-4 spherical aluminum ~ 9 micron [13], AlB2 – aluminum diboride ~ 8 micron. AlB2f is the same aluminum diboride with a polymeric coating by fluorine-substituted aliloxisilane (FAOS, the same as coating material named "A4" in [14]). The mass fraction of coating in diboride amounts to about 4 %, particle size is about 4 micron. The listed above mean sizes D_{43} calculated using the data obtained with the Malvern 3600E sizer are given for powder fuels. APf is a fine fraction of ammonium perchlorate with specific surface of 5400 cm^2/g. AP is the sieve fraction of ammonium perchlorate with the particle sizes of 250-315 micron.

Table 1: Component composition (% mass) of model propellants

Propellant	**Binder**	**B**	**Al**	**AlB2**	**AlB2f**	**APf**	**AP**
12B	20.00	11.99	-	-	-	22.67	45.34
18B	20.78	17.82	-	-	-	20.80	40.60
24B	23.53	23.52	-	-	-	17.65	35.30
40B	30.50	37.57	-	-	-	10.33	21.60
40AB	30.50	-	-	37.50	-	10.67	21.33
40ABF	30.50	-	-	-	36.00+1.5[a]	10.67	21.33
21A17B	31.19	16.54	20.51	-	-	10.59	21.17

[a] 4 % of FAOS in diboride amounts to 1.5 % in the 40ABF propellant

As follows from the table, the following systematic variations of formulations were performed:

- Formulations 12B, 18B, 24B, 40B – a gradual increase in boron content from 12 % to 40 %. The real content values are shown in Table 1.
- Formulation 40AB – a complete substitution of nominal 40 % of boron in formulation 40B by 40 % of aluminum diboride.
- Formulation 40ABF – similarly, but the substitution of boron by modified aluminum diboride with FAOS coating.
- Formulation 21A17B – the substitution of 40 % of boron by the "aluminum diboride imitator", i. e., a mechanical aluminum-boron mixture of the mass ratio as in aluminum diboride.

The experiments were performed with the non-cured paste-like mixtures, placed in Pyrex glasses of 10 mm in diameter and of 15 mm depth, in nitrogen at pressures of about 1.2 MPa and 2.5 MPa. An original technique for sampling the condensed combustion product (CCP) was used [15] (a "variant with a check valve" [16]). In addition to the sampling, the setup allows estimating the burning rate from the pressure versus time record. The particles were frozen near the specimen surface at a distance of 20–30 mm. One of the technique advantages is the high (close to 100%) representativeness (efficiency) of sampling the particles of any size due to the combination of stack of metallic sieve screens and analytical aerosol filter as a trap.

The sampled CCP particles were subjected to morphological, particle size, and chemical analyses. A morphological analysis was performed using an optical microscope, and in some cases, a scanning electron microscope (SEM) Merlin|VP Compact (Zeiss) with an EDS-device X-Max^N (Oxford Instruments) for local element analysis (EDS – energy dispersive spectroscopy). The experiments indicate that after firing test the inner parts of the bomb are covered with white sediment consisting of small particles. From the appearance and location of the sediment we concluded that it was B_2O_3, resulting from condensation upon dilution of the combustion products with cool, inert

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gas. Of interest are the dark (almost black) irregular spots observed within the white sediment. The CCP particles were extracted from the bomb by several methods. The *samples* produced were named as following:
Cleaning – the dry cleaning with brush all the inner bomb elements, including the stack of sieves after its disassembly.
Wash_off – the washing of the same elements with acetone (after dry cleaning) followed by acetone evaporation at room temperature in the Petri dish.
Carcass – the residue in the glass after sample burning extracted with a brush, figure 1

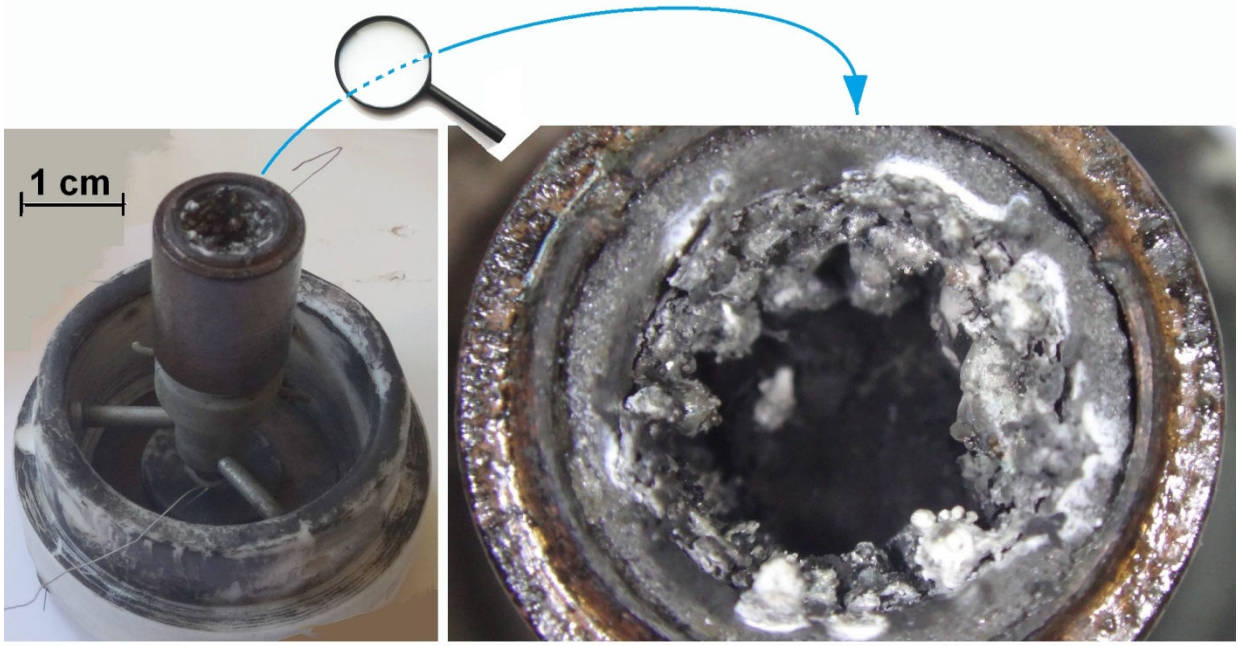

Figure 1: Left – the photographic image of cover with mounted specimen holder – Pyrex glass in the bronze cartridge. Right– the magnified view of *carcass* residue in glass after burning. Propellant 40AB, pressure 2 MPa.

Filter – after the experiment, the AFA filter was dried at room temperature for 24 h, and weighted. Its additional weight caused by the particles captured was recorded. The filter or its fragments were then dissolved in acetone and a suspension underwent a granulometric analysis with a Malvern 3600E sizer.
Fractions – for the propellants 40AB, 40ABF, and 21A17B, the CCP particles obtained by the dry *cleaning* were fractionized: < 160 micron, 160-315 micron, 315-500 micron, and > 500 micron, using miniature sieves. The fraction exceeding 500 micron was conditionally named as 500–1000 micron.
Sometimes, for the propellants with boron, 12B and 18B, the particles obtained by the dry *cleaning* were washed in the hot distilled water, filtered and dried on a paper filter. The washing is assumed to remove boron oxide because of its water solubility and to leave the agglomerated boron particles. These washed samples were called *black*.

All the samples were weighted using analytical scales with an error of ±0.0001 g. The samples *cleaning, wash_off, fraction < 160 micron, black*, and *filter* were analyzed on the "Malvern 3600E" sizer in acetone. In all cases, the suspension was ultrasound treated for 30 s before measurements. During the measurements it was mechanically stirred; the measurements were repeated in three minutes; the results were averaged.
The particle size analysis results were presented as a joint (by the samples *cleaning, wash_off, filter*) histogram of the size-distribution density function f(D) of the relative CCP particles mass. The distribution function was used to calculate the momentum based mean D_{mn} sizes using generally accepted formulas [15, 16].
The chemical analysis was performed by cerimetric method [17] to determine the so-called "reducing" number RN, which characterizes the reducing ability of samples, i. e., their oxidation capability [18]. The reducing number may be considered as an "effective mass content" of the active "unoxidized substance" in the sample under study. In the general case, the combustion efficiency of the boron-containing fuel η may be determined as

$$\eta = (M_{ccp} \cdot RN_{ccp})/(M_{prop} \cdot RN_{prop}) = (M_{ccp} \cdot RN_{ccp})/(M_{prop} \cdot mf \cdot RN_{mf}),$$

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where M_{ccp} and M_{prop} are the masses of CCP and propellant, respectively, RN_{ccp}, RN_{prop}, and RN_{mf} are, respectively, the reducing numbers for CCP, propellant, and metallic fuel components introduced into the propellant, mf is the mass fraction of metallic fuel component in the propellant. The number RN_{mf} was determined preliminarily by cerimetric analysis. It equals 10.6 for Al, 22.1 for B, 16.1 for AlB2, and 13.6 for AlB2f. Note that to apply the formula correctly, one should know the total mass of CCP, M_{ccp}, which requires the high sampling representativeness.

Using the data on propellant composition and the experimental values of sample masses (*cleaning, wash_off, carcass, filter, fractions*) and dividing by M_{prop} we determine the following dimensionless parameters:
m_{mf} is the total, dimensionless fuel mass in the propellant ($m_{mf} \equiv$ mf),
m_s is the dimensionless mass of residues in the glass (*carcass*),
m_{ccp} is the dimensionless CCP mass (*cleaning*+*wash_off*+*filter*, is calculated without the residue in the glass),
CCP = $m_{ccp} + m_s$ is the total, dimensionless CCP mass (*cleaning* + *wash_off* + *filter* + *carcass*),
CCPt is the total, dimensionless, theoretical CCP mass, calculated assuming the complete transformation of both B into B_2O_3 with stoichiometric coefficient of 3.22 and Al into Al_2O_3 with stoichiometric coefficient of 1.89.
The parameter CCP/CCPt is the ratio of the collected CCP mass and its maximal, theoretical value which indirectly characterizes the combustion efficiency of the metallic fuel, because the technique used to CCP sampling exhibits the high representativeness.
$E = (1-\eta)\cdot m_{mf}\cdot RN_{mf}$ is a comparative efficiency of energy release.

3. Experimental results

The main results are summarized in Table 2. For the burning rate, the confidence intervals correspond to the instrumental measurement error, caused by mainly to a small sample length. A statistic error related to the reproducibility of the burning rate in repeated tests is substantially less. For the mass parameters m_{ccp}, m_s, CCP/CCPt, and η the value of standard deviation Se is ±0.01…±0.03, and in one case only (propellant 18B, 2.5 MPa) parameter η= 0.53±0.07.

Table 2: Burning rate *r*, mass CCP parameters, and combustion inefficiency η

Propellant	***p*, MPa**	***r*, mm/s**	$\mathbf{m_{ccp}}$	$\mathbf{m_s}$	**CCP/CCPt**	**η**
12B	1.1	12.4±0.3	0.28[a]	0.01	0.73	0.34
	2.5	23±1	0.36	0.02	0.94	0.26
18B	1.2	16±1	0.46	0.02	0.79	n\a
	2.5	22±1	0.47	0.02	0.82	0.53
24B	1.2	11±1	0.60	0.02	0.82	0.61
	2.3	18±1	0.57	0.04	0.82	0.64
40B	1.2	7±1	0.73	0.03	0.63	0.82
	2.4	8.7±0.5	0.88	0.05	0.77	0.70
40AB	1.2	5.5±0.2	0.38	0.20	0.62	0.70
	2.2	7.5±0.2	0.39	0.05	0.62	0.70
40ABF	1.2	8.8±0.6	0.36	0.24	0.67	0.73
	2.3	9.0±0.3	0.41	0.19	0.67	0.73
21A17B	1.2	5.9±0.5	0.30	0.21	0.56	0.62
	2.2	8.7±0.5	0.45	0.24	0.64	0.61

[a] in this experiment the filter was damaged, and the particles were lost; n\a – no data

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3.1 Burning rate

As follows from Table 2: (1) The burning rates of the propellants containing about 40 % of the metallic fuel are comparable for each pressure levels. (2) The burning rate of the propellants with boron decreases with increasing boron content in the range from 12 % to 40 %. In this case, for the compositions 18B, 24B, and 40B the dependency is close to the linear one, figure 2.

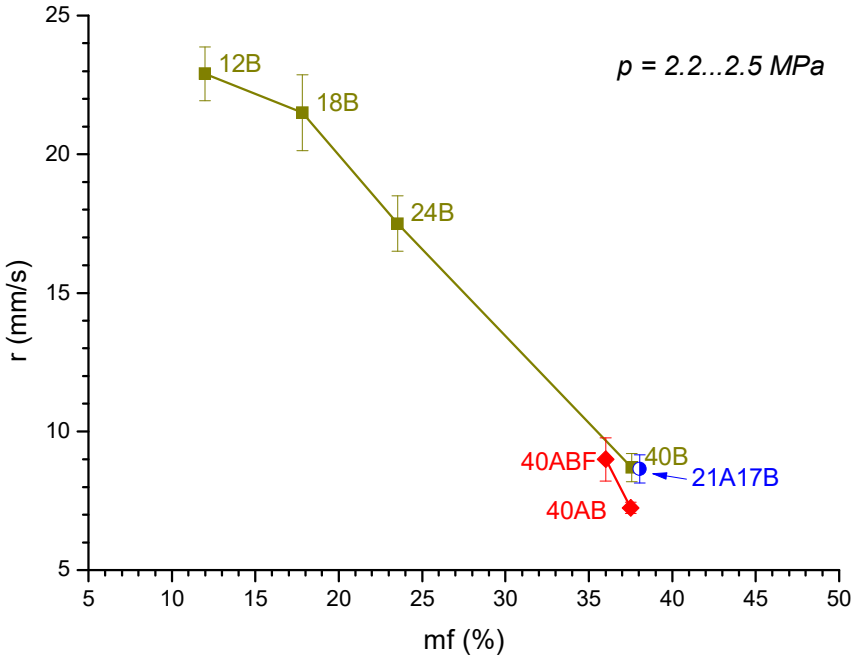

Figure 2: The dependency of the burning rate *r* at a pressure of ~ 2.3 MPa on the content of the metallic fuel in the propellant mf.

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3.2 CCP of propellants with boron

Figure 3 shows the CCP appearance of propellant 18B, sampled at a pressure of ~ 2.5 MPa. Most of the particles are of micron and submicron size.

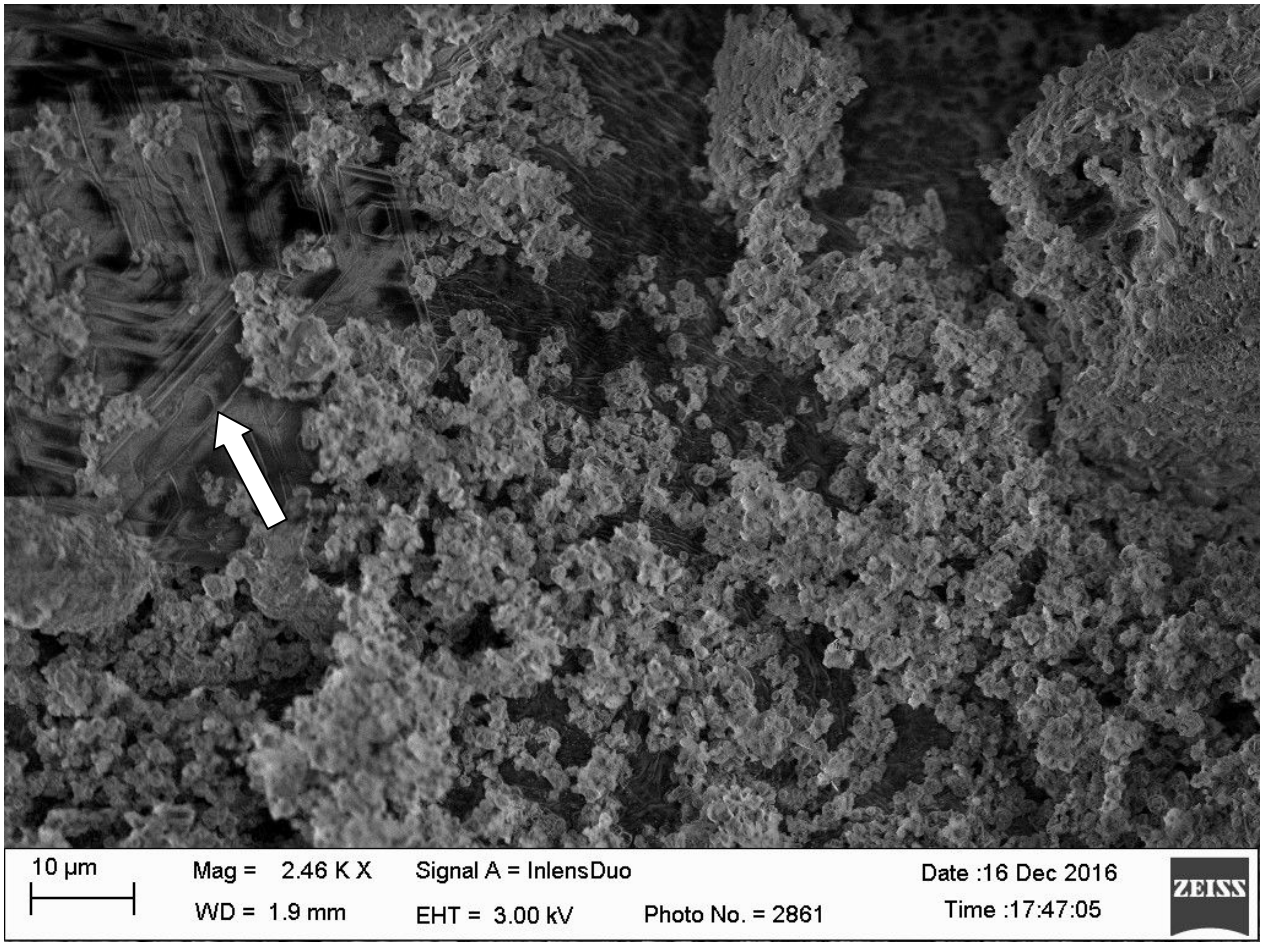

Figure 3: The SEM-image of the CCP particles sediment for the propellant 18B with boron only (sample *cleaning*). There are the scaly formations with the terraces of growth typical of crystallization (marked with arrow).

The sediment of the CCP particles from the experiments with the propellant 12B at 2.5 MPa was washed out in a hot water to extract boron agglomerates (particles *black*), as described above. The SEM-images of these particles are presented in figure 4.

The EDS-analysis performed at two arbitrary points indicates boron contents of 99.12 and 99.36 at. %. So these particles actually are real boron agglomerates. As follows from figure 4, many particles are of either teardrop or even spherical shape, which testifies to, at least, a partial boron melting. The surface of particles is “porous” (with cavities) which is likely to be due to the washing-out of oxide. The dazzling white regions indicate the local, dielectric properties and represent, probably, the insoluble alternative combustion products.

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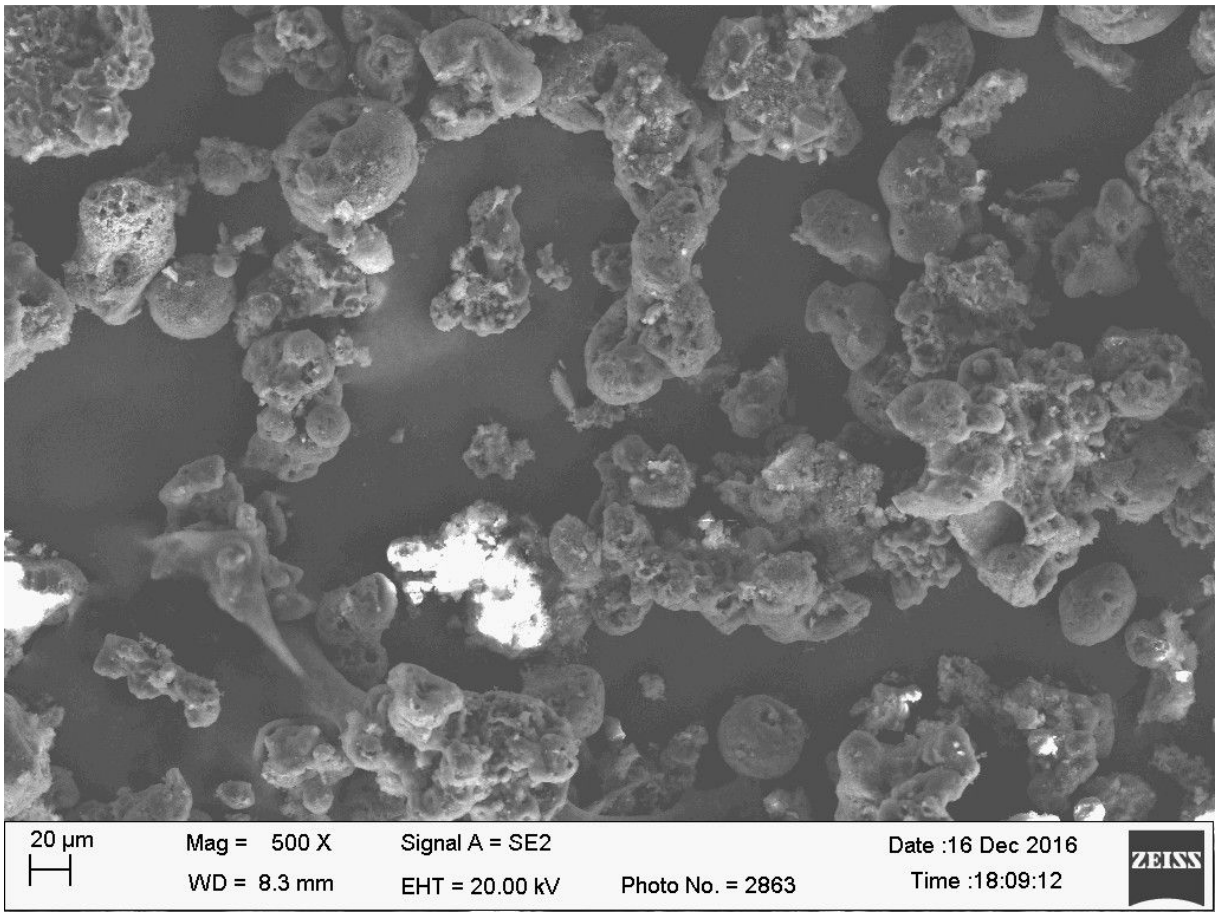

Figure 4: The SEM-photo of washed boron agglomerates (particles *black*).

Table 3 summarizes the mean sizes of the CCP particles and of the washed agglomerates from experiments with propellant 12B at 2.5 MPa and those of the initial boron. The agglomerate size D_{43} exceeds the size D_{43} of the initial boron by order of magnitude.

Table 3: Mean particle sizes D_{mn}

D_{mn}, micron →	D_{10}	D_{20}	D_{30}	D_{43}	D_{53}
Initial boron	2.9	2.9	2.9	3.0	3.1
Boron agglomerates (*black*)	3.9	5.0	7.0	28.6	36.7
CCP (*cleaning*)	3.9	5.1	7.2	32.2	40.7

3.3 CCP of the propellants with boron and aluminum

Analyzing the distribution function and the morphology of the CCP particles one indicates that the presence of aluminum in the system (both in diboride and as a mechanical mixture component) causes the intensification of agglomeration, observed as the increase in both the CCP particles size and the mass of residues in the glass (parameter m_s in Table 2).

Figure 5 shows the large agglomerates formed by the combustion of propellant 40AB at 2.1 MPa and the results of their elemental analysis. At the four points analyzed, the ratio between oxygen and aluminum atoms amounted to 1.76, 2.12, 2.43, and 2.16 as compared with 1.5 for the stoichiometric aluminum oxide. It is of interest that no boron signal was found which indicates that boron is “encapsulated” and covered by aluminum oxide.

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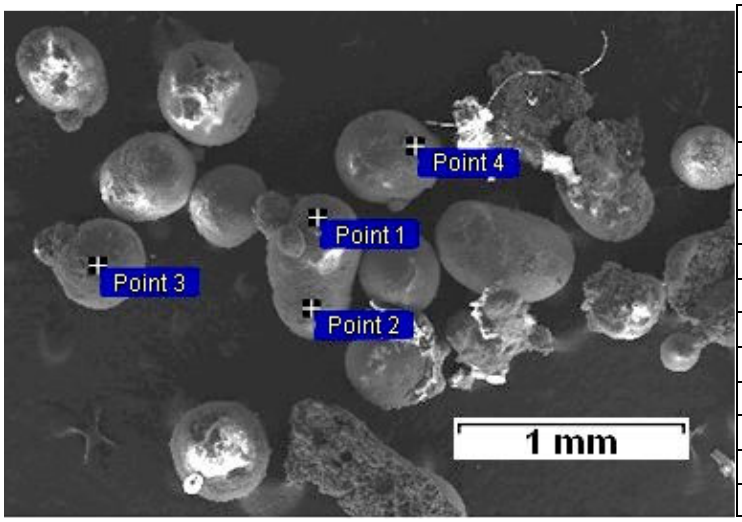

Element	Atomic % at points 1…4			
	1	2	3	4
N	-	-	-	5.75
C	6.74	8.48	10.42	-
O	57.10	61.42	62.20	51.18
F	3.42	0.80	1.45	15.76
Al	32.46	29.04	25.61	23.71
P	0.10	0.13	0.13	0.09
Cl	0.05	-	0.04	3.02
Ag	0.13	0.12	0.11	0.09
Fe	-	-	0.04	0.15
Si	-	-	-	0.19
Sc	-	-	-	0.03
Cu	-	-	-	0.04
Re	-	-	-	0.01

Figure 5:The CCP particles of fraction 315-500 micron of the propellant 40AB, sampled at 2.1 MPa. The points and EDS data on the local content of chemical elements.

Of particular interest is the efficiency of energy release $E = (1-\square)\cdot m_{mf}\cdot RN_{mf}$, figure 6. This definition of E assumes that all the fuels exhibit the same heat release per unit mass. Remember also that the CCP particles were frozen near the surface of a specimen.

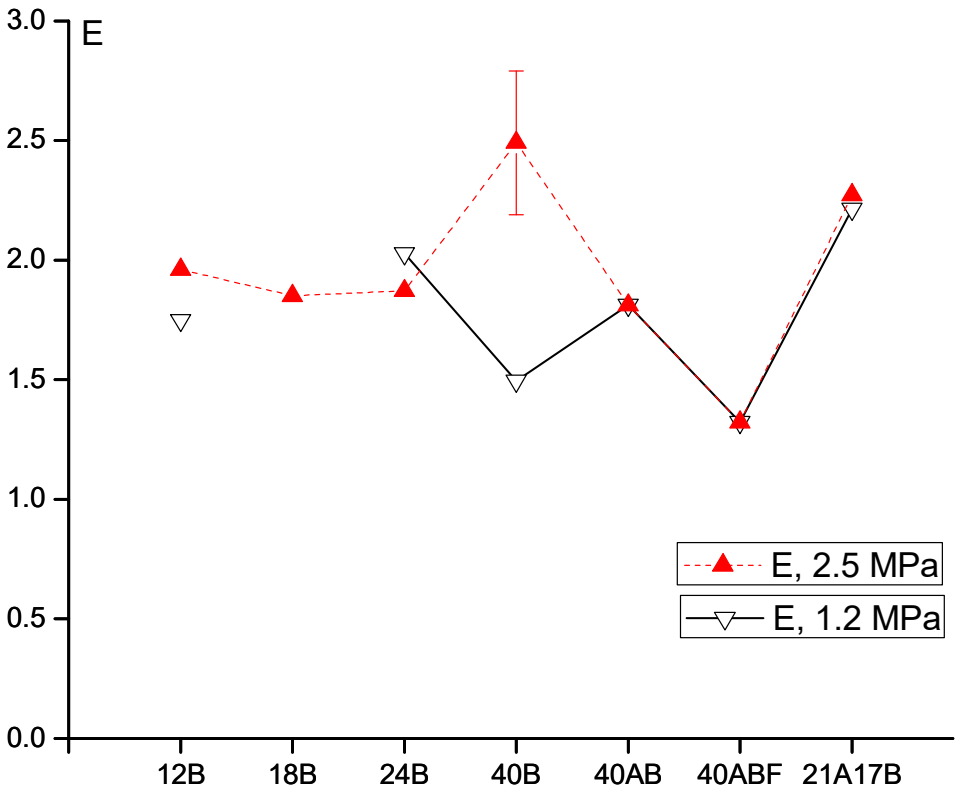

Figure 6: Parameter E at two pressure levels for propellants under study (abscissa). The confidence interval (maximal) is shown for one point. The error is due to the inaccuracy in the determination of combustion inefficiency.
The analysis of figure 5 revealed the following.

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1. The highest value of E is recorded for the propellant 40B at 2.5 MPa. It is quite possible that the propellants with the higher amount of boron are more energy effective.

2. For the propellants with diborides and the aluminum diboride imitator (40AB, 40ABF, 21A17B), the points, corresponding to pressures of 1.2 MPa and 2.5 MPa, have practically coincided.

3. The efficiency for propellant 40ABF (FAOS coating) is not higher than that for propellant 40AB. This is due to both the larger combustion incompleteness for propellant 40ABF and the lower initial value of the reducing number for the AlB2f fuel.

4. The propellant 21A17B with the imitator demonstrates surprisingly high energy release efficiency.

4. Conclusions and future work

It has been established that the condensed combustion products (CCP) of boron-containing fuels are composed mainly of agglomerated boron and boron oxide. Oxide white residue represents the aggregates consisting of submicron particles. The boron agglomerates are dark and have either the teardrop or spherical shape which testifies to the partial melting of boron. The size of agglomerates exceeds the particle size of initial boron by order of magnitude. Substituting boron by either aluminum diboride or aluminum diboride with FAOS coating has failed to provide the increase in both the combustion efficiency and the energy release efficiency. The presence of aluminum in the combined fuels intensified agglomeration which, in turn, caused the increase in the size of CCP particles and in carcass mass (residues in the glass). In this case, a mechanical boron-aluminum mixture demonstrated comparatively high combustion efficiency and energy release efficiency.

The future investigations of the combustion characteristics of propellants with higher boron content, with polyborides (e. g., AlB_{12}) and mechanical mixtures (Al + B) with varying Al/B ratio seem rather promising.

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