Ignition and combustion characteristics of propellants containing coated aluminum particles

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Abstract

The effect of coating the aluminum particles with different polymers on the ignition and combustion characteristics was studied for 6 propellant formulations at pressure near atmospheric. The propellants had identical formulation {18 % Al, 18 % AP 160-315 μm, 9 % AP S=6700 cm^2/g, 35 % HMX 100-800 μm and 20% an energetic binder (polyvinyl tetrazole polymer plasticized with nitroester)}. The reference propellant contained commercial non-coated aluminium powder with size D_{43} ~ 10 μm, other propellants contained coated aluminium. Ignition time at constant heat flux, power spectrum of the recoil force oscillations in self-sustaining combustion, burning rate, and agglomeration parameters were examined. It was found that the coating materials slightly affect the ignition and the frequency spectrum of the combustion process. The action of different coatings on the agglomeration process was found to be complex and unexpected - decreasing the agglomerate size can be accompanied by decreasing the completeness of aluminium conversion into oxide.

Introduction

It is known that the promising way to modify the metal particles ignition and combustion behavior is the coating of their surface with different type materials - oxide, other metal, oxidizer, polymer, etc. [1]. For instance, some fluorine-containing polymers provide an increase in the flame propagation velocity for heterogeneous system *aluminum particles* + *gaseous oxidizer* [2-3]. This fact allows expecting the effect of the fluorine-containing coated aluminum on propellant combustion characteristics and the solid motor performance. The goal of the present work was detailed characterization of the combustion characteristics of propellants containing aluminum particles with different coatings. The ignition delay time, burning rate, frequency spectrum of the recoil force, and intensity of agglomeration were examined at atmospheric pressure for 6 propellant formulations.

Theoretical background

The designations of used aluminum powders are shown in table 1. The reference powder is A1, which is pure aluminum. All other powders are prepared via coating A1 with different organic compounds, mainly (except A5) fluorine containing.

Table 1. Aluminum powders under study

Aluminum powder	Coating matter	Propellant ID
A1	no coating	Y1
A2	$Si[OCH_2(CF_2-CF_2)_3H]_4$	Y2
A3	$Cl_2Si[OCH_2(CF_2-CF_2)_2H_2]_2$	Y3
A4	$(CH_2=CH_2-O)_2Si[OCH_2(CF_2-CF_2)_2H_2]_2$	Y4
A5	$CH_2=C(CH_3)(COOCH_3)$	Y5
A6	$CH_2=CF(COOCH_3)$	Y6

The series of calculations were performed using thermodynamic equilibrium code ASTRA [4] to estimate the influence of the coating matter on the energetic parameters of propellant combustion. All calculations were made for some model propellant having elemental formula $C_{9.89}H_{38.97}N_{5.94}Al_{6.65}O_{23.31}Cl_{5.78}$. The mass fraction g_c of coating matter was varied in the range 0÷5 % of the aluminum mass content. The effect of the coating matter was characterized in terms of the combustion temperature T_f, vacuum specific impulse I_{sp}, and mass fraction of condensed phase in the combustion products Z_k. Table 2 presents the listed parameters calculated at g_c = 5% (i. e. when 5% of aluminum mass in propellant is replaced with coating matter).

Table 2. Thermodynamic calculation data (at g_c = 5%)

	A1	A2	A3	A4	A5	A6
T_f, K	3359	3360	3358	3352	3329	3344
I_{sp}, m/s	2734	2738	2738	2737	2733	2735
$Z_к$	0.309	0.301	0.301	0.302	0.306	0.305

The effects of the total amount of coating matter on the relative change in the value of specific impulse, $\delta I_{sp}=100\%*(I_{sp}-I^o_{sp})/I^o_{sp}$, and on the relative change of the value of condensed phase fraction in combustion products, $\delta Z_k=100\%*(Z_k-Z^0_k)/Z^0_k$, are shown in figures 1 and 2. Here upper index "0" corresponds to the value calculated at g_c = 0.

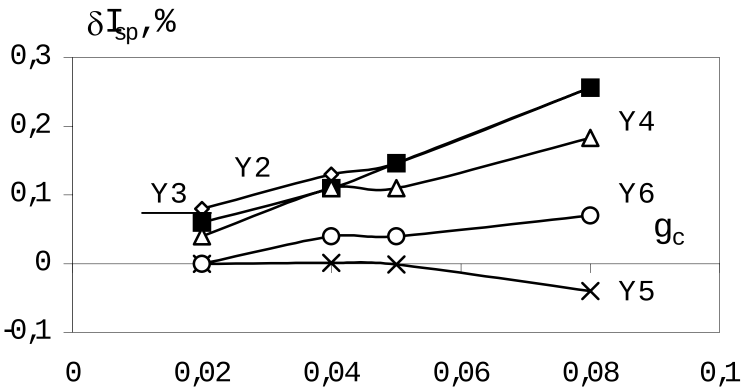

Figure 1: Variation of specific impulse magnitude δI_{sp} *vs* g_c (mass fraction of the coating matter in Al powder).

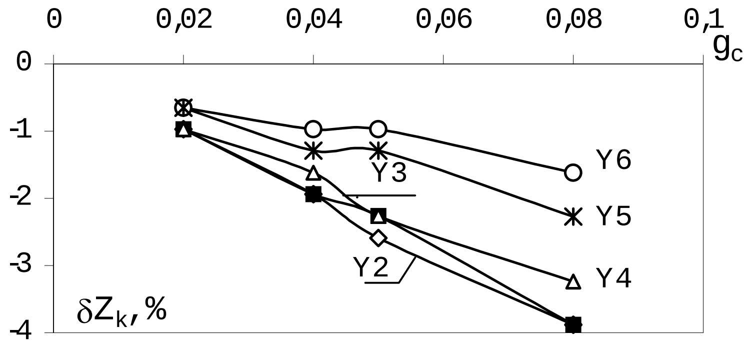

Figure 2: Variation of magnitude of the condensed phase fraction in combustion products δZ_k *vs* g_c (mass fraction of the coating matter in Al powder).

The calculated thermodynamic data show that the coating matter theoretically may play positive role in improving the solid propellant combustion efficiency via increasing specific impulse and decreasing the mass fraction of condensed combustion products.

Experimental results

Propellant samples. The effect of coating the aluminum particles with different polymers on the combustion characteristics was studied for 6 propellant formulations Y1÷Y6 identical to those in [5]. Numerical index of propellant coincides with index of aluminum powder used, see table 1. Aluminum A1 is commercial non-coated powder with characteristic grain size D_{43} = 10 μm. All propellants were manufactured using well characterized ingredients and included by weight 18 % Al, 27% AP (9 % AP1 S=6700 cm^2/g plus 18 % AP2 160-315 μm), 35 % HMX (100-800 μm) and 20% energetic binder (polyvinyl tetrazole polymer plasticized with nitroester) [6]. The aluminum powders have identical particle size distribution with the only difference being the type of aluminum coating. The chemical analysis of aluminum powders performed as described in [7], showed that in all powders A1÷A6 the active (metallic) aluminum content was 96.8÷98.0 % and the total aluminum content was 98.6÷99.8 %. Thus, the mass fraction of coating in the aluminum powder rather small (< 1%). More details regarding particle size analysis of propellant components upon propellant manufacturing can be found in [5].

Samples for the firing tests had cylindrical shape with diameter equal to approximately 8 mm and with the length of 17 mm. Lateral surface was inhibited with Solprein®. Propellant density estimated via measuring the weight and sizes of cured samples was 1.70÷1.74 g/cm^3.

Burning rate and agglomeration characteristics. The original method for quenching and sampling the condensed combustion products (CCP) in flow through bomb [8] was used to measure agglomerate characteristics. In present work experiments were performed at initial pressure 1 gauge atmosphere. Characteristic (mean) pressure was 1.5 atm (for the reference, experiments in [5] were made at 44 atm). The mean burning rate was calculated as the sample length divided by the burn out time. The last one was derived from the record of photodiode signal obtained in course of the firing test. The photodiode was placed inside the bomb to measure the light emission from burning sample. Burning rate data are presented in figure 3. One can see that the burning rate for propellants Y3, Y4, Y5 practically coincides with that for the reference propellant Y1. Propellant Y2 have reduced and propellant Y6 have enhanced burning rate as compared with the reference propellant.

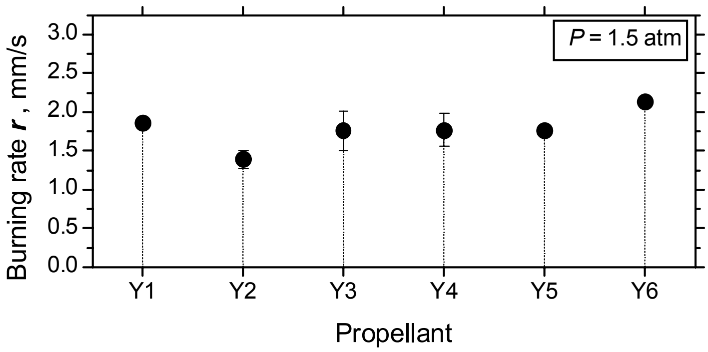

Figure 3: Burning rate at pressure 1.5 atm.

Sampled CCP particles were subjected to particle size and chemical analyses. Detailed description of treatment procedures is given in [5, 8]. All propellants under study ***at pressure 1.5 atm obey the strong agglomeration scenario***. Its typical features are: big size of agglomerates and their significant fraction in total mass of CCP, and relatively high incompleteness of aluminum combustion [9]. In present work the CCP particles with size greater than 80 μm are considered as agglomerates[*]. The **mass distribution function** for agglomerates is presented in figure 4 in the form of relative mass:
$f_i(D) = m_i / (M_{prop} \cdot \Delta D_i)$, where m_i is the mass of CCP in the i-th histogram size interval, M_{prop} is the mass of propellant burned, and ΔD_i is the width of i-th size interval. The **mean sizes of agglomerates D_{mn},** which characterize a consolidation of the aluminum particles in the combustion wave, are given in table 3.

*) The wire sieve with mesh size 80 μm was used for preliminary screening the sampled particles. The value of screen mesh size in the size range 60-100 μm does not affect the results of experimental data processing since the mass distribution function has local minimum in this size range. The CCP particles to the right of the minimum are agglomerates, the CCP particles to the left of the minimum are oxide (smoke) particles.

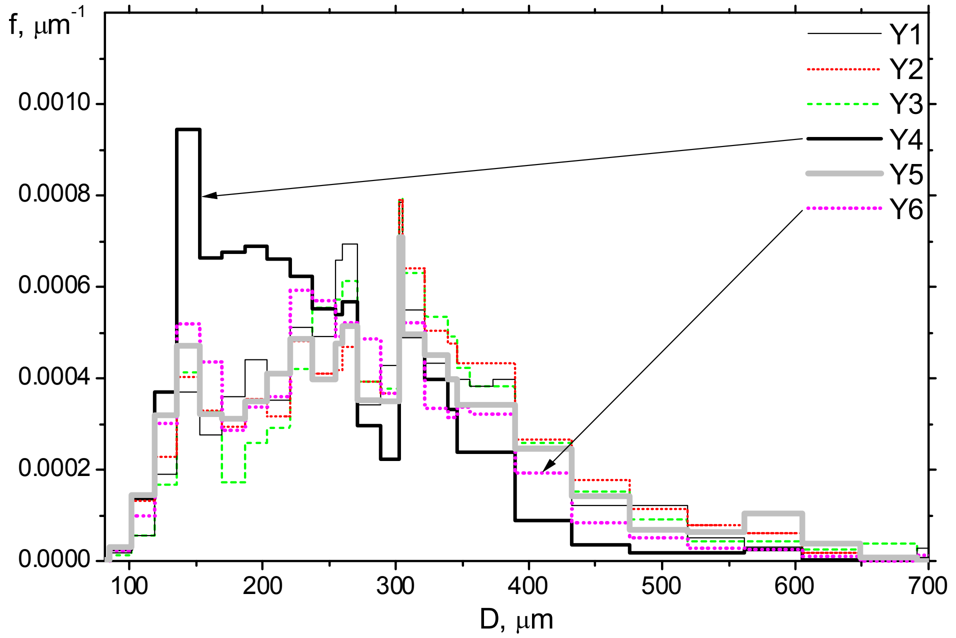

Figure 4:

Mass size distribution function for agglomerates sampled at pressure 1.5 atm.

Table 3.

Agglomerate mean size D_{mn} (μm) calculated in the size range (80 μm - D_{max})

Propellant	D_{10}	D_{20}	D_{30}	D_{21}	D_{32}	D_{43}	D_{53}
Y1	195	209	226	225	262	304	326
Y2	185	202	220	220	262	307	328
Y3	197	213	230	230	269	310	330
Y4	170	179	190	189	213	246	266
Y5	177	193	211	210	253	305	332
Y6	180	193	207	207	240	278	298

By analyzing figure 4 one can see that the shape of curves for mass size distribution functions for propellant Y1, Y2, Y3, and Y5 are similar and they close in value. The curves corresponded to the propellant Y6 and especially Y4 (pointed with arrows in figure 4) demonstrate different behavior that results in smaller value of mean sizes, table 3. For instance, D_{43} = 304-310 μm for propellants Y1, Y2, Y3, Y5, but D_{43} = 246 μm for Y4 and D_{43} = 278 μm for Y6.

The agglomeration behavior of the propellant Y4 looks most attractive. In this case the coating matter does not affect the burning rate but suppress the agglomeration process and reduces the size of agglomerates. However, not only size distribution characterizes the combustion efficiency of the metal in propellant formulation [10-13]. Let us consider other parameters – **dimensionless agglomerate mass $\mathbf{m_{ag}}$** that stands for the propellant's tendency to form a slag residue in the motor chamber, and **incompleteness of the aluminum combustion** η that stands for the propellant's capability to release a heat upon aluminum conversion into oxide. The following definitions were used to calculate these parameters: $\mathbf{m_{ag} = M_{ag}/M_{prop}}$ (experimentally determined agglomerate mass M_{ag} scaled by the mass of propellant burned M_{prop}); $\boldsymbol{\eta = m^{Al}_{ccp}/m^{Al}_{prop}}$, where m^{Al}_{ccp} is dimensionless (also scaled by M_{prop}) mass of metallic (unburned) aluminum in CCP, $m^{Al}_{prop} \equiv 0.18$ is dimensionless initial mass of aluminum in propellant. The mass of unburned aluminum in CCP was determined by permanganatometric method [7]. Figures 5 and 6 exhibit the interdependence of aforementioned parameters D_{43}, m_{ag}, η. Positive correlation between values η and m_{ag} exists for all propellants, figure 5. It is known [10-12], that for readily agglomerating propellants the unburned aluminum is amassed mainly in agglomerate particles ($m^{Al}_{ag} \approx m^{Al}_{ccp}$). Therefore, when increasing m_{ag}, incompleteness of aluminum combustion increases.

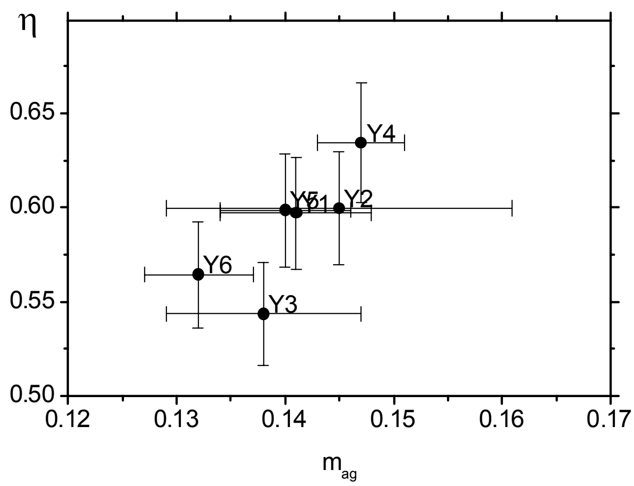

Figure 5:
Correlation between dimensionless agglomerate mass m_{ag} and incompleteness of aluminum combustion η.

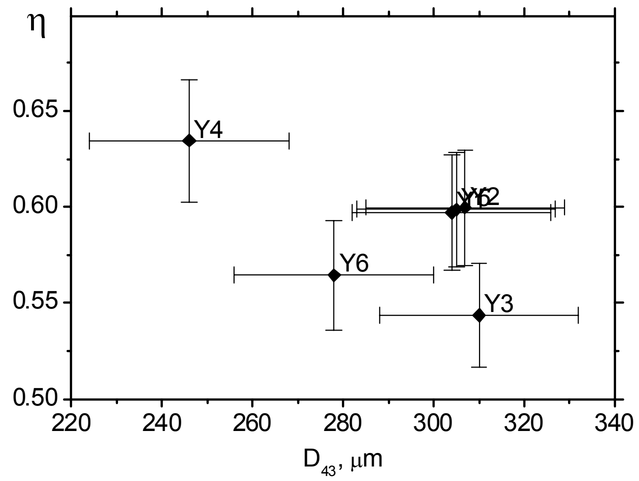

Figure 6: Incompleteness of aluminum combustion η *versus* mean agglomerate size D_{43}.

Figure 6 represents the dependence of incompleteness of aluminum combustion on mean agglomerate size D_{43}. One can see that there is no direct correlation between η and D_{43}. Aluminum combustion completeness is found to be similar for propellants Y1, Y2, Y5 (points are situated very close), slightly better for propellants Y6 and Y3, but some worse for propellant Y4. Note that indicated features can not be explained by difference in the burning rate which is maximal for propellant Y4 and minimal for propellant Y2, see figure 3.

It is interesting to note that the propellant Y4 having the value of burning rate the same as the reference propellant Y1, is characterized by minimal agglomerate size and maximal incompleteness of aluminum combustion as compared with other tested propellants. Thus, in the case of propellant Y4 the coating matter not only suppresses the coalescence of the aluminum particles but also prevents them against the oxidation.

Ignition under constant heat flux

Experiments on ignition were performed using 5-kW xenon lamp with radiant flux equal to 16 cal/(cm^2·s). The ignited sample surface was blackened with the lamp soot. It was found that the **ignition delay times for all propellants are close in value** and equal to 0.22±0.03 s. DTA data obtained at heating rate 10 K/min show that all propellants start decomposing fast at the temperature 160-180^{o}C (probe weight 200 mg, air, platinum crucible). This indicates that the thermal behavior of binder may specify conditions for propellant ignition.

Frequency analysis of reactive force signal

The frequency analysis of the propellant burning rate was made by processing the signal of the recoil force (RF) recorded by the capacitance-type force transducer. The experimental technique for measuring RF is described in [13].

The dependence of RF (F) on the burning rate r is given by expression

$$F = (1-\eta)kr^n , \qquad (*)$$

where ŋ is the dispersion degree, and k is the matching coefficient. The magnitude of exponent n depends on the propellant type and combustion conditions. Usually the value of n is close to 2 [14].

The transducer used had dynamic registration range equal to 64 dB at the noise level equal to 3 mg. The signal from transducer was magnified and digitized via use of 10 bite DC. Sampling time of acquisition system was equal to 0.4 ms that allowed recording frequencies up to 1250 Hz. The ignition of the propellant samples was performed by the radiant flux from 5 kW Xenon lamp. Experimental set up is described in [15].

Because the present work aimed only for comparative analysis of the frequency parameters of the burning rate, the exact values of the parameters in expression (*) were not determined. The analysis was performed using direct records of the RF.

Figure 7 presents an example of the RF signal record for propellant Y_1. To perform the frequency analysis, the middle part of the signal curve has to be chosen. The chosen part of the signal curve is processed at first for extracting the mean value and then the transient component of the signal is analyzed by the Fourier transform method. It results in obtaining the power spectrum of the signal, the examples of which for Y_1 and Y_2 propellants are shown in figure 8a. It is easily recognized the noisy character of the primary analysis data. The smoothed power spectrum curves for all propellants studied are shown in figure 8b. These curves can be divided into two groups (Y_1, Y_4, Y_5 and Y_2, Y_3, Y_6, respectively) regarding the maximal level of the power spectrum function.

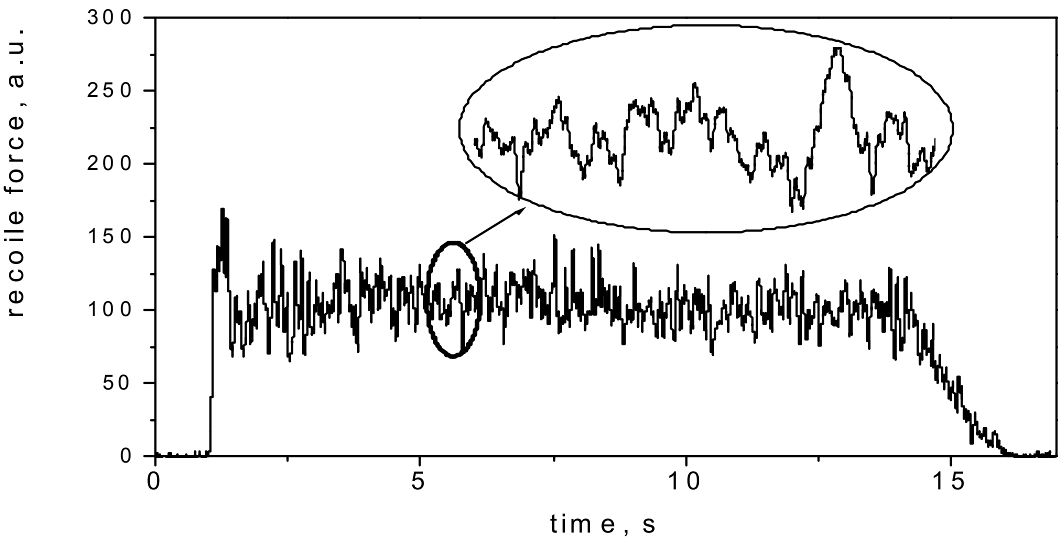

Figure 7: Example of recoil force signal record for Y1 propellant

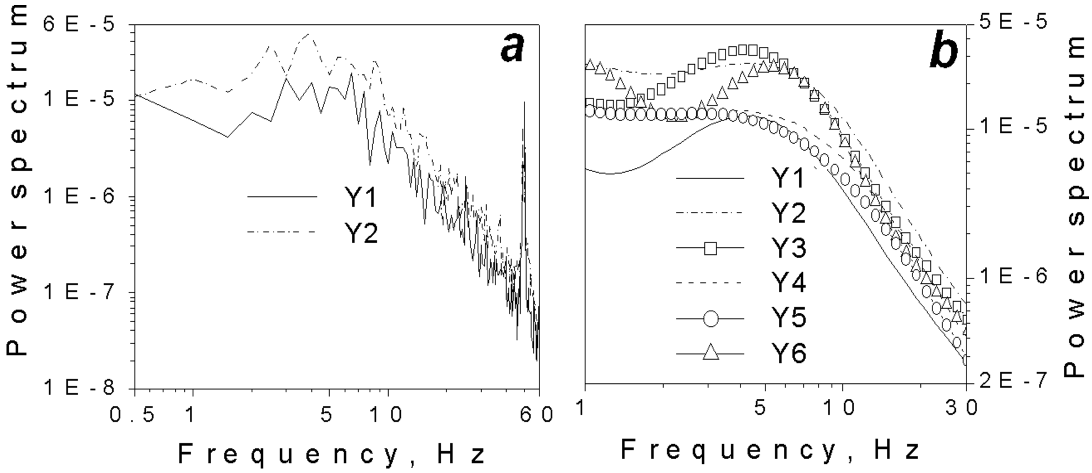

Figure 8: a - Examples of experimental power spectrum (Y1 and Y2);
b - Approximation of experimental power spectrums (Y1 - Y6).

It has to be underlined that due to restricted sensitivity the force transducer can not distinguish the disturbance generated by influence individual metal particle (agglomerate). Therefore, the recorded RF signal is the result of action of the finite ensembles of ejected particles. In addition, time resolved RF signal contains low frequency amplitude variations caused by transient combustion of coarse particles of AP and HMX. It is seen in figure 8b that the amplitude of the power spectrum function quickly decreases when the frequency exceeds 8 - 10 Hz. Rough estimation shows that this frequency boundary corresponds to particle size 0.18 – 0.23 mm.

Conclusions

The effect of coating the aluminum particles with different polymers on the ignition and combustion characteristics was studied for 6 propellant formulations at near atmospheric pressure. All propellants were of the same formulation (18 % Al, 18 % AP 160-315 μm, 9 % AP S=6700 cm^2/g, 35 % HMX 100-800 μm and 20% an energetic binder - polyvinyl tetrazole polymer plasticized with nitroester). Reference propellant contained non-coated aluminium powder A1 with size D_{43} ~10 μm, other propellants contained same size coated aluminium.

When studying the intensity of agglomeration of aluminum coated with different polymers, it was revealed the following. Aluminum **A2** coated with $Si[OCH_2(CF_2-CF_2)_3H]_4$ provides decreasing the burning rate while aluminum **A6** coated with $CH_2=CF(COOCH_3)$ provides increasing the burning rate. Use of aluminum **A4** coated with $(CH_2=CH_2-O)_2Si[OCH_2(CF_2-CF_2)_2H_2]_2$ results in sizable reduction of the agglomerate size without increasing the burning rate, but makes worse the completeness of aluminum combustion. Aluminum **A3** coated with $Cl_2Si[OCH_2(CF_2-CF_2)_2H_2]_2$ and aluminum **A5** coated with $CH_2=C(CH_3)(COOCH_3)$ provide better completeness of the metal combustion without changing the agglomerate size. Aluminum **A6** coated with $CH_2=CF(COOCH_3)$ increases the completeness of aluminum combustion with simultaneous reduction of agglomerate size.

The recoil force frequency analysis did not allow determining the correlation between the agglomeration behavior and the recoil force power spectrum for the propellants studied. However, the preliminary estimations show that the effect of agglomerates formation and ejection from the burning surface can become distinguishable at certain conditions. Therefore, it will be necessary in the future to conduct detailed studies for different type propellants and varied combustion conditions aimed for establishment of such correlation.

The aluminum coatings tested did not affect the ignition delay time at heat flux of 16 cal/(cm^2·s).

The experimental data obtained show that the variation of only aluminum coating matter can modify some of important characteristics of solid propellant combustion. The action of coating on aluminum agglomeration is thought to be complex and ambiguous. Therefore their practical use requires the optimization based on more detailed investigations.

Acknowledgments

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