DOI: 10.13009/EUCASS2017-105

Formation of solid residues in combustion of boron-containing solid propellants

S A Rashkovskiy
Institute for Problems in Mechanics of the Russian Academy of Sciences
Vernadskogo Ave., 101/1, Moscow, 119526, Russia

Abstract

The model of the boron particles agglomeration in combustion of boron-containing solid propellants is suggested. The process of the boron particles agglomeration is considered as a result of competition between two main processes: the formation of adhesive bonds between contacting boron particles and rupture of these bonds under the action of gaseous combustion products. The criterion of solid residues formation and dependence of their relative mass on pressure are obtained. It is shown that depending on the propellant burning rate law, two different types of propellants with different behavior of the agglomeration process at pressure change can exist.

1. Introduction

Boron–containing solid propellants which have an oxidizer deficit and a high content (up to 30% by weight and more) of boron are considered as the promising propellants for the ducted rockets. Such solid propellants are capable to self-sustained combustion and their combustion occurs in a special gas generator. Due to low content of oxidizer, such propellants are characterized by incomplete conversion of fuel components (primarily, binder and boron) which leads to residues (slag) formation. Moreover, the temperature of the combustion products in the chamber of the gas generator is typically less than 2000K. At this temperature, the boron particles are in solid state and weakly react with the oxidizing components of the solid propellant. Combustion products of the solid propellant flow out of the gas generator through the nozzle into the secondary combustor in which air is fed from the environment. In the secondary combustor, combustion of the boron particles and other condensed products occurs in oxygen of air. Most part of the energy which is used to creation of the thrust is released during the combustion of condensed products (primarily, boron particles) in air flow in the secondary combustor. For this reason, the efficiency of the ducted rocket is largely determined by the completeness of the boron particles combustion in the secondary combustor. Taking this in mind, the design of the ducted rocket is directed to obtain a maximum efficiency of boron combustion [1-3].

For theoretical estimation of the completeness of boron combustion in secondary combustor, the data obtained in the experiments on ignition and combustion of the single boron particles are usually used. However, there are direct and indirect data indicating that combustion of the boron-containing propellants is accompanied by an intense agglomeration of the boron particles near the burning surface. As a result, the coarse conglomerates (aggregates) containing a lot of primary boron particles leave the propellant burning surface [4]. We use the term “conglomerate” with respect to boron particles instead of the term “agglomerate” which is adopted in the literature when describing the process of agglomeration of aluminum particles on the burning surface of solid propellant. This highlights a fundamental difference in the structure of the boron particles conglomerates from aluminum particles agglomerates [5].

The interferometric measurements [6] showed that the particles with sizes of 20-200 μm leave the burning surface of the boron-containing propellant, although the initial boron particles in propellant have usually the sizes of 1-2 μm.

In [7], it was observed an irregular combustion of propellant with high boron content (40-50%) with a periodic variation in burning rate level with a detachment of unburned layers. An increase in the size of the conglomerates, detached from the burning surface, was observed at pressures above 50 atm.

Experiments [1,2] showed that boron combustion efficiency in the same secondary combustor can vary from 0.6 up to 0.95, depending on the organization of the air flow and flow of solid propellant combustion products in the secondary combustor. It is significantly less than the estimations obtained from the models of combustion of single boron particles which are in propellant. The experimental data [1,2] indirectly indicate the presence of the boron particles conglomerates in combustion products of the boron-containing solid propellant. The combustion time of the

DOI: 10.13009/EUCASS2017-105

boron particles conglomerate can significantly exceed the combustion time of single primary boron particle due to the difference in their sizes and to the essentially difference in the ignition and combustion behavior of the conglomerates compared to single boron particle. The experiments [1,2] demonstrate an ability to control the combustion time of the boron particles conglomerates due to optimization of a design of the secondary combustor.

An ignition of the boron particles conglomerates in air for different sizes of the primary boron particles and different diameters and densities of the conglomerate was investigated experimentally in [8]. It was found out that the ignition temperature of a conglomerate substantially less than the ignition temperature of single boron particles (~1000 K vs ~1900 K). Experimental data [8] showed that the conglomerate ignition temperature varies with their density monotonically and at a certain conglomerate density, the ignition temperature reaches a minimum. Decrease in the ignition temperature of the conglomerate compared to single boron particle is a positive factor contributing to the completeness of the boron combustion in the secondary combustor of the limited length. At the same time, the combustion time of the conglomerate is essentially long compared to that of single boron particles, thus the total time required for ignition and complete combustion of the conglomerate is significantly longer (at the same conditions) than the time required for complete combustion of the single particles entering the conglomerate.

Note that the agglomeration of the boron particles in ducted rockets plays more important role than the agglomeration of aluminum particles in conventional solid rocket motors, because, in ducted rockets, the incompleteness of boron combustion, connected with a formation of conglomerates, leads to significant additional (along with the two-phase losses) decrease in the specific impulse (down to 20%).

The main way of reducing the size of the conglomerates entering the secondary combustor from the gas generator is a reducing the intensity of the boron particles agglomeration on the burning surface of solid propellant. This can be achieved by optimizing the composition and structure of solid propellant.

For effective reducing the agglomeration of the boron particles on the burning surface, we need a clear understanding of the mechanisms of this complicated process and identification of the controlling factors, by changing of which one can control the intensity of the agglomeration.

Moreover, for the correct calculation of the ignition and combustion behavior of the conglomerate, one needs to know not only its size but also its structure and shape that can significantly affect these processes.

In contrast to the detailed studies of the agglomeration of aluminum particles, in the literature, there is very little of the experimental data on the boron particles agglomeration in combustion of the boron-containing solid propellants.

Some experimental study of the agglomeration of refractory powders was done in the work [9].

In the works [10,11], the condensed combustion products of boron-containing propellant was investigated experimentally. The propellant formulation was 19.0% hydroxyl-terminated polybutadiene (HTPB), 4.0% dioctyl sebacate (DOS), 4.0% catocene, 34.0% ammonium perchlorate (AP), 26.0% boron powder, 7.5% magnesium powder, 4.0% aluminium powder and 4.5% toluene-2,4-diisocyanate (TDI). Initial boron particles in propellant have the sizes about 1μm. It was shown that the condensed-phase products mainly consist of B, C, B_4C (or $B_{12}C_2$), BN, Mg, MgO, $MgAl_2O_4$, Al, Al_2O_3, $AlCl_3$, $NH_4[Mg(H_2O)_6]Cl_3$, NH_4Cl and Fe_3O_4; there were large amounts of boron oxide and boron carbide in the condensed-phase products, which indicates that elemental boron is highly active during the combustion process in gas generator. The content of elemental boron decreases significantly with an increase in chamber pressure and this is mainly due to the production of boron carbide, but the content of boron oxide does not increase simultaneously.

Considerable quantities of CO are produced at low chamber pressures and the content of CO decreases significantly with an increase in chamber pressure. The composition of the combustion products shows that carbon exists mainly in the form of boron carbide, carbon and carbon monoxide at low chamber pressures, while it exists mainly as boron carbide and carbon at high chamber pressures. Boron carbide is produced by the reactions of elemental boron with binder’s hydrocarbons (CH_4, C_2H_4, and C_4H_6), so a decrease in CO may be the result of the higher reactivity of elemental boron and binder’s hydrocarbons.

The content of unreacted boron in the condensed-phase products decreased exponentially while the content of boron carbide increased with the increase in chamber pressure [11].

The burning rate of propellant plays an important role in the consumption of elemental boron and production of boron carbide. The reaction of elemental boron cannot reach the chemical equilibrium because of a short reaction time; therefore, the composition of boride was strongly affected by the burning rate of the propellants: the higher the burning rate, the lower the reaction percentage of boron when the residence time was the same.

Experimental data [10,11] showed that a decrease in the unreacted boron correlated with an increase in boron carbide.

Illustrative result is the dependence of the mean size of conglomerates leaving the burning surface on pressure: for some compositions, the mean size of conglomerates increases with increasing pressure, while for others it decreases [11]. This indicates the existence of several competing mechanisms that control the process of formation of condensed-phase products in combustion of boron-containing solid propellants. For the last case it was found that most of the boride in the condensed-phase combustion products is either elemental boron or boron carbide particles

DOI: 10.13009/EUCASS2017-105

produced with a longer time; therefore, the large particle size may result from the agglomerated boron or boron carbide at a higher temperature.

The goal of this work is to develop a model of the residues formation (primarily, the boron particles agglomeration) in combustion of the boron-containing propellants, and to identify the factors that govern the process.

2. Mechanism of solid residues formation

The mechanism of boron particles agglomeration is largely similar to the mechanism of aluminum particles agglomeration in combustion of composite solid propellants [12], but it has its own features [5]. As in the case of aluminum, the boron particles agglomeration is connected with the presence of contacting particles in the condensed phase of the propellant. At passing of a heat wave in the propellant, a conversion of its components (binder, oxidizer particles etc.) and simultaneously a heating of the boron particles occur. In contrast to aluminum particles which melting point is less than the temperature of the propellant burning surface, boron has a melting point above the temperature of the propellant burning surface, and even higher than the temperature of the combustion products in the gas generator and therefore boron is always present at solid state on the propellant burning surface. The boron particles, located in propellant are covered with a thin film of boron oxide B_2O_3. The boron oxide melting point ($T_{m\mathrm{B}_2\mathrm{O}_3} = 720K$) is commensurable with a temperature of the propellant burning surface ($T_s = 700 - 1000\ K$) and considerably less than a temperature of combustion products of the propellant in a gas generator ($T_b = 1500 - 2000\ K$). This means that the boron particles on the propellant burning surface have the liquid oxide film and contacting particles are bound by the liquid bridge of B_2O_3. If the contacting boron particles did not have the oxide film or it was insufficiently thick to create the liquid bridge between the particles after its melting, the sintering of the particles can occur due to their rapid heating in the propellant burning wave. Furthermore in the vicinity of the contact of the particles, the various chemical compounds can form due to the chemical reactions of the species of the products of decomposition of solid propellant both between themselves and with boron. In particular, the sufficiently strong boron carbide B_4C and boron nitride BN can be formed. In [10,11,13] have shown that for HTPB-based solid propellants, a significant increase in B_4C content with increasing pressure is observed, at that at low pressures, there is a marked deviation from thermodynamic equilibrium, while at high pressures, the B_4C concentration approaching to equilibrium. The GAP-based propellants demonstrate the opposite behavior [13]: for these propellants, the content of boron carbide in the combustion products decreases with increasing pressure. Results of [10,11,13] showed that the boron carbide can be predominant boron compound on the burning surface of the propellant and directly above the surface. The strong chemical compounds which are formed in the vicinity of the contact points of the boron particles can create the mechanical (adhesive) bonds between the particles.

Due to oxidizer deficit in the boron-containing solid propellants, the incomplete conversion of the binder occurs on the burning surface which leads to formation of condensed-phase products consisting, primarily, of carbon. This slag forms the skeleton layer on the propellant burning surface which creates the additional bonds holding the boron particles on the burning surface and promoting their agglomeration.

As a result of all these processes, the condensed-phase products form on the propellant burning surface the coral-like structures, which have the different shapes, sizes and porosity [7]. Gaseous combustion products of decomposition of easily degradable components of propellant, affect these coral-like structures, creating an aerodynamic detached force. This force depends on the shape, size and porosity of the coral-like structure on the propellant burning surface and increases in average with increasing the size of these structures. When the detached aerodynamic force becomes greater than the adhesive force which binds the skeleton layer with the burning surface, the breaking of the bonds occurs and conglomerate is detached from the burning surface.

As a result, the conglomerates consisting of a plurality of interconnected primary boron particles being in solid state come into the propellant combustion products. Note that unlike the aluminum particle agglomerates which are almost spherical drops [9] consisting of molten aluminum and solid aluminum oxide, the boron particles conglomerates are the porous structures consisting, essentially of the solid boron, boron carbide and carbon [11]. The structure of the propellant is a determining factor in formation of the boron particles conglomerates [5].

The mechanism of agglomeration, described above, imposes certain limitations on the methods of simulation of the boron particles agglomeration. For example, the pockets model [14-18] can be used in some cases for calculation of the aluminum particles agglomeration, but it quite inapplicable in order to calculate the boron particles agglomeration because the conglomerate can unite the boron particles belonging to different, sometimes separated by a considerable distance, “pockets”.

With some modifications, the statistical model [19-21] developed for the aluminum particles agglomeration and considering the process in dynamics can be used for calculation of the boron particles agglomeration. But the method of the direct numerical simulation of the agglomeration [12] is more appropriate for this purpose. This method consists in modeling the solid propellant structure [22,23] and the subsequent calculations of the behavior of each boron particle near the propellant burning surface, taking into account changes in its thermal and chemical states and

DOI: 10.13009/EUCASS2017-105

accounting its mechanical interaction with the gaseous combustion products and with other boron particles. The method [12] was applied to simulation of boron particle agglomeration in combustion of boron-containing solid propellants [5].

3. Model of the boron particles agglomeration

In general the propellant burning rate u as well as the boron particles conglomerates size depend on the propellant structure. This means that changes in the composition and structure of the propellant lead to a simultaneous change in the burning rate and in the intensity of the agglomeration process. Obviously, a complete model of combustion of boron-containing solid propellant should take into account both the effect of burning rate on agglomeration process and the effect of agglomeration process on the burning rate. In [5], a simplified approach was used in which the propellant burning rate is considered to be given and only the calculations of the boron particles agglomeration are performed. This is due to the fact that the propellant burning rate can be easily determined experimentally, while the measurement of sizes of the boron particles conglomerates which are formed during the propellant combustion is much more complicated problem. For this reason, it is appropriate to estimate the sizes, shape and structure of the conglomerates by calculation using a model of the agglomeration process and the experimentally determined propellant burning rate.

Boron particle agglomeration is considered as a result of competition between two main processes: the formation of adhesive bonds between contacting boron particles and rupture of these bonds under the action of gaseous combustion products.

At low Reynolds numbers, which corresponds to the flow above the burning surface, the force $\mathbf{f}_i$ acting on the i-th particle from the side of gaseous combustion products flowing from the burning surface can be written in the form

$$\mathbf{f}_i = \mu(\mathbf{U}_i - \mathbf{V}_i) \tag{1}$$

where $\mathbf{V}_i$ is the velocity of i-th boron particle; $\mathbf{U}_i = (U_i, 0, 0)$; U_i is the velocity of the gaseous combustion products, flowing from the burning surface under i-th boron particle; μ is some coefficient (“aerodynamic drag” coefficient of the particle) which is considered as a matching coefficient of the model.

Due to heterogeneity of the propellant, the velocity U_i will be different in different points of burning surface. As an approximation, one can consider the mean velocity of the gaseous combustion products: $U_i = U$,

$$U = (1 - m_r)\frac{\gamma}{\rho}u \tag{2}$$

where m_r is the mass fraction of condensed-phase products of decomposition of propellant on the burning surface; γ is the propellant density, $\rho = \frac{p}{RT_{as}}$ is the density of gaseous combustion products, p is pressure; T_{as} is a characteristic temperature of gaseous combustion products above the burning surface, e.g. $T_{as} = 0.5(T_s + T_b)$.

The adhesive force between contacting particles i and k prevents their detachment can be written in the form [5]

$$\mathbf{F}_{ik} = K_{ik}\frac{\mathbf{r}_k - \mathbf{r}_i}{|\mathbf{r}_k - \mathbf{r}_i|}\left(|\mathbf{r}_k - \mathbf{r}_i| - \frac{1}{2}(D_i + D_k)\right) \tag{3}$$

where K_{ik} is the factor characterizing the rigidity of the bonds between contacting particles i and k; D_i is the diameter of i-th particle. Further, the factor K is considered to be the same for all pairs of interacting particles, i.e. $K_{ik} = K$ and is considered to be a matching coefficient of the model.

In this case, the equations that describe the behavior of the boron particles above the burning surface have the form [5]

$$\frac{d\mathbf{r}_i}{dt} = \frac{K}{\mu}\sum_k \frac{\mathbf{r}_k - \mathbf{r}_i}{|\mathbf{r}_k - \mathbf{r}_i|}\left(|\mathbf{r}_k - \mathbf{r}_i| - \frac{1}{2}(D_i + D_k)\right) + \mathbf{U}_i \tag{4}$$

Each bond has a tensile strength F_{ik}^0: if the tearing force (3) exceeds the tensile strength, the breaking of the bond between the particles i and k occurs, and this particles will cease to interact. The tensile strength of the particles bonds is a random variable that depends on many factors: the nature of the particles connection, the temperatures of

DOI: 10.13009/EUCASS2017-105

the particles and ambient gas, the ambient gas composition, the duration of the particle stay in the flow of gaseous combustion products (time elapsed since the release of these particles on the burning surface), etc. All these factors are not currently studied, so for all pairs of particles, we take the same value of F_{ik}^0 equal to F^0 which will be considered to be a mean strength of the bonds between the contacting particles.

Condition of the breaking of the bonds is as follows [5]

$$|\mathbf{r}_k - \mathbf{r}_i| > \frac{1}{2}(D_i + D_k) + F^0/K \tag{5}$$

For analysis of the model, one can introduce the nondimensional variables, keeping for $\mathbf{U}$, $\mathbf{r}_k$ and t the previous notations. We choose the characteristic size of the boron particles D_0 as a characteristic spatial scale, the solid propellant burning rate u as a characteristic velocity scale and the ratio D_0/u, as the characteristic time scale. Then nondimensional diameter of the boron particle is $d = D/D_0$. As follows from (2), the nondimensional velocity of the gaseous combustion products near the burning surface

$$\mathbf{U} = \left((1-m_r)\gamma/\rho, 0, 0\right) \tag{6}$$

The system of equations which describes in nondimensional variables the behavior of the boron particles above the propellant burning surface, takes the form

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{U}_i + \varepsilon \sum_k \xi_{ik} \frac{\mathbf{r}_k - \mathbf{r}_i}{|\mathbf{r}_k - \mathbf{r}_i|}\left(|\mathbf{r}_k - \mathbf{r}_i| - \frac{1}{2}(d_i + d_k)\right) \tag{7}$$

where ξ_{ik} = 0 if the condition

$$|\mathbf{r}_k - \mathbf{r}_i| > \frac{1}{2}(d_i + d_k) + \delta \tag{8}$$

was satisfied at any preceding time for particles *i* and *k*, i.e. they never contacted or the breaking of the bond already occurred; otherwise ξ_{ik} = 1; if at some point in time, there was a collision of the particles *i* and *k* which did not contact previously, i.e. the condition $|\mathbf{r}_k - \mathbf{r}_i| \le \frac{1}{2}(d_i + d_k)$ was satisfied, we assume ξ_{ik} =1 until the condition (8) will satisfy; this allows taking into account the emergence of new adhesive bonds between boron particles in the course of their movement;

$$\varepsilon = \frac{KD_0}{\mu u} \tag{9}$$

$$\delta = \frac{F^0}{KD_0} \tag{10}$$

Besides the parameters characterizing the propellant structure (content and dispersity of the components), the model (7)-(10) contains three nondimensional parameters: δ, ε and U which can vary independently of each other when changing the propellant composition and combustion conditions. Nondimensional velocity of the gaseous combustion products near the burning surface U (2) is considered to be known, because the density of the gaseous combustion products near the burning surface can be calculated with sufficient accuracy, either thermodynamically or using the temperature near the burning surface measured in experiments. However, the parameters K and μ, and therefore, the parameters ε and δ cannot be calculated at present from the first principles and should be considered as the matching coefficients. However, some information about the nature of changes of the parameters ε and δ can be obtained from their definitions.

Let the propellant burning rate is described by the power law

$$u = u_0 (p/p_0)^{\nu} \tag{11}$$

where u_0 and ν are the constant parameters of the propellant which are considered to be known.

DOI: 10.13009/EUCASS2017-105

Then one can write

$$\varepsilon = \varepsilon_0 (p/p_0)^{-\nu} \tag{12}$$

$$U = U_0 (p/p_0)^{-1} \tag{13}$$

Where

$$\varepsilon = \frac{KD_0}{\mu u_0} \tag{14}$$

$$U_0 = (1 - m_r) \frac{\gamma}{\rho_0} u \tag{15}$$

$$\rho_0 = \frac{p_0}{RT_{as}} \tag{16}$$

It can be expected that the strength of the interparticle bonds δ will depend on the residence time of particles in the heated layer of the condense phase of propellant $\tau = \kappa/u^2$ (κ is the thermal diffusivity of the condensed phase of propellant): the longer the boron particles are in heated layer of the propellant condensed phase, the stronger the bonds are established between them due to forming the liquid boron oxide bridges and strong chemical compounds formed at chemical reactions between the propellant species. We assume that the dependence of the strength of adhesive bonds between the boron particles on the residence time of the particles in the heated layer of the propellant condense phase can be described by the power function: $\delta \sim \tau^{\alpha}$. In this case one obtains

$$\delta = Au^{-2\alpha} \tag{17}$$

where A and $\alpha > 0$ are the constants.
Then one can write

$$\delta = \delta_0 (p/p_0)^{-2\alpha\nu} \tag{18}$$

Where

$$\delta_0 = Au_0^{-2\alpha} \tag{19}$$

is the constant.
If the dependencies of the parameters K, μ, F^0 and T_{as} on pressure are weak, then the expressions (12), (13) and (18) completely determine the dependence of the boron particles agglomeration process on pressure.
Although, the parameters ε_0, U_0 and δ_0 do not depend on the pressure, they can be varied due to changing the composition of the propellant (the content and dispersion of the components, the types of the binder and oxidizer, etc.). Furthermore, it is obvious that any surface coating of the boron particles, which leads to a decrease in their mutual adhesion (for example, easily removed coating) will contribute to a reduction of the coefficient δ_0 and hence to a reduction of the intensity of the agglomeration process. For example, in [24], combustion of the micron-size boron particles (average particles diameter ~51μm) covered with glycidyl azide polymer (GAP) was investigated in a hot gas flow of a flat-flame burner and in composite solid propellant. The results [24] show that propellants containing the amorphous boron particles coated with GAP, demonstrate a higher burning rate and a lower intensity of agglomeration compared to the base composition containing the uncoated boron particles.
Obviously, an intense agglomeration is possible only if the coefficient ε satisfies the condition

$$\varepsilon\delta > U \tag{20}$$

Otherwise the single boron particles will leave the burning surface and agglomeration will not occur.
Using (12), (13) and (18), one can rewrite the condition (20) in the form

$$\varepsilon_0 \delta_0 (p/p_0)^{-(1+2\alpha)\nu} > U_0 (p/p_0)^{-1} \tag{21}$$

DOI: 10.13009/EUCASS2017-105

From this inequality, it follows that two different kinds of propellants are possible:
A. The propellants which have

$$(1+2\alpha)\nu < 1 \qquad (22)$$

For example, for $\alpha = 1$ this corresponds to $\nu < 0.33$.
In this case the condition (21) takes the form

$$(p/p_0)^{1-(1+2\alpha)\nu} > \frac{U_0}{\varepsilon_0\delta_0} \qquad (23)$$

It follows that there is a threshold pressure p_a:

$$p_a/p_0 = \left(\frac{U_0}{\varepsilon_0\delta_0}\right)^{\frac{1}{1-(1+2\alpha)\nu}} \qquad (24)$$

such that there is no agglomeration at $p < p_a$ while the agglomeration occurs when $p > p_a$ and it is amplified with increasing pressure.
B. The propellants which have

$$(1+2\alpha)\nu > 1 \qquad (25)$$

For example, for $\alpha = 1$ this corresponds to $\nu > 0.33$.
In this case the condition (21) takes the form

$$(p/p_0)^{(1+2\alpha)\nu-1} < \frac{\varepsilon_0\delta_0}{U_0} \qquad (26)$$

It follows that there is a threshold pressure p_b:

$$p_b/p_0 = \left(\frac{\varepsilon_0\delta_0}{U_0}\right)^{\frac{1}{(1+2\alpha)\nu-1}} \qquad (27)$$

such that there is no agglomeration at $p > p_b$ while the agglomeration occurs when $p < p_b$ and it is amplified with decreasing pressure.
Thus, theoretically, there may exist two different types of boron-containing propellants, depending on their composition which are different by a behavior of the agglomeration at pressure change: for some propellants (with low ν) agglomeration increases with increasing pressure, while for the others (with high ν) it increases with decreasing pressure. This conclusion is supported by the available experimental data [10,11].
Results of numerical simulation of boron particle agglomeration are given in [5].

4. Critical conditions for the slag formation

It has been experimentally established that a layer of condensed-phase residues (slag) forms on the burning surface of boron-containing propellants, under certain conditions. In some cases, these residues represent a porous skeleton layer on the burning surface, but in some cases, the residues can completely fill the combustion chamber of the gas generator.
Experimental data show that for some propellants, the residues are formed at high pressures (above some critical pressure p_{cr}, which is a characteristic of propellant), but no residues are formed at low pressures ($p < p_{cr}$). For other propellants, on the contrary, the residues are formed at low pressures ($p < p_{cr}$), while at high pressures ($p > p_{cr}$), the combustion products of the propellant are completely take away from the combustion chamber of the gas generator.

DOI: 10.13009/EUCASS2017-105

This result completely corresponds to the analysis carried out above, in particular, to the relation (21).
To determine the critical pressure p_{cr}, we can use equation (21), writing it in dimensional form.
The same result can be obtained by considering the detachment of the skeleton layer (slag) formed on the burning surface.
Assuming that this layer is porous and the gaseous products of decomposition of the propellant components are filtered through it, for detachment force we obtain the expression

$$F_r = 3\pi\beta N\mu_g VdhS$$

where $N = \frac{6}{\pi d^3}(1-\varepsilon)$ is the number of particles of condensed phase per unit volume of slag; ε is the porosity of the slag; h is the thickness of the slag layer; d is the characteristic diameter of the particles of the particles in the slag (it is of order of the pore sizes); S is the area of the slag layer; μ_g is gas viscosity, depending on temperature; β is a coefficient of order unity.
The mass of gaseous products filtered through the slag per unit time $\varepsilon\rho VS$ is equal to the mass input of the gaseous combustion products of propellant $(1-m_r)\gamma uS$; u is the burning rate of propellant; γ is the density of propellant; ρ is the density of the gas.
Thus

$$V = \frac{(1-m_r)}{\varepsilon}\frac{\gamma}{\rho}u$$

Taking into account that $p = \rho RT$, one obtains

$$F_r = \frac{18\beta(1-m_r)}{d^2}\frac{(1-\varepsilon)}{\varepsilon}\frac{\gamma\mu_g RT}{p}uhS$$

The strength of adhesion of the slag layer to the burning surface (and slag layers among themselves)

$$F_c = \sigma_s \frac{\pi d^2}{4}NSd$$

where σ_s is the strength of the slag (the stress at which the bond between the particles in the slag breaks down).
We take

$$\sigma_s = B\tau^{\alpha}T^{-\beta}$$

where α, β, B are the factors depending on the propellant properties.
The dependence of σ_s on the residence time of particles in the heated layer of the condense phase of propellant $\tau = \kappa/u^2$ has been discussed above (see (17)). The dependence σ_s on temperature reflects the fact that the strength of the slag layer decreases with temperature increase.
Then

$$F_c = B\tau^{\alpha}T^{-\beta}\frac{3(1-\varepsilon)}{2}S$$

The condition for detachment of slag from the burning surface has the form $F_r > F_c$ or

$$12\beta(1-m_r)\frac{\gamma\mu_g RT}{pd^2}uh > B\varepsilon\tau^{\alpha}T^{-\beta}$$

This allows finding the maximum thickness of the slag layer on the burning surface

DOI: 10.13009/EUCASS2017-105

$$\frac{h_{\max}}{d} = \frac{\varepsilon B \kappa^{\alpha} d}{12\beta\gamma R} \frac{p}{u^{1+2\alpha}} \frac{T^{-(1+\beta)}}{(1-m_r)\mu_g}$$

If $\frac{h}{d} \sim 1$, then we can believe that the slag is not formed. Then the condition for the absence of slag will have the form

$$(1-m_r)\frac{u^{1+2\alpha}}{p}\mu_g T^{(1+\beta)} > A_0 \tag{28}$$

where $A_0 = \frac{\varepsilon B \kappa^{\alpha} d}{12\beta\gamma R}$ is the parameter that can be considered a constant characteristic of propellant.

If we assume that $\mu_g T^{(1+\beta)} \approx const$ (i.e., we do not take into account the temperature changes at the burning surface with the pressure), and take the burning rate law in the form (11), then the condition (A1) can be written in the form

$$(p/p_0)^{(1+2\alpha)\nu - 1} > \frac{A_0 p_0}{(1-m_r)\mu_g T^{(1+\beta)} u_0^{1+2\alpha}}$$

which completely corresponds to the relation (21), which determines the conditions of intensive agglomeration.
We again come to the conclusion that for propellants A that satisfy the condition (22), the residues are formed at pressures greater than p_{cr} and grow with increasing pressure, while for $p < p_{cr}$ the residues are not formed for these propellants, where

$$p_{cr}/p_0 = \left[\frac{(1-m_r)\mu_g T^{(1+\beta)} u_0^{1+2\alpha}}{A_0 p_0}\right]^{\frac{1}{1-(1+2\alpha)\nu}} \tag{29}$$

In particular, for these propellants, p_{cr} increases with increasing u_0, which can be regulated by additives with practically no changes in the composition and structure of propellant.
On the other hand, for propellants B that satisfy the condition (25), the residues are formed at pressures less than p_{cr} and grow with decreasing pressure, while for $p > p_{cr}$ there is no residues for these propellants, where

$$p_{cr}/p_0 = \left[\frac{A_0 p_0}{(1-m_r)\mu_g T^{(1+\beta)} u_0^{1+2\alpha}}\right]^{\frac{1}{(1+2\alpha)\nu - 1}} \tag{30}$$

For these propellants, p_{cr} decreases with increasing u_0.
Comparison with experimental data shows that $\alpha = 1$.

5. Dependence of the mass of residues on mean pressure in gas generator

Experiments show that the relative mass of slag remaining in the combustion chamber after the end of the gas generator operation depends on the mean pressure during the operation of the gas generator.
We assume that the pressure in the combustion chamber increases with time (progressive diagram) according to a linear law: $p = p_1 + at$, where p_1 is the initial pressure; $a > 0$.
Let us consider the case of propellants A that satisfy the condition (22), when the slag is formed if the pressure in the combustion chamber exceeds the critical pressure (29).
Then the slag is not formed at $p \le p_{cr}$. The instant of operation of the gas generator, up to which the slag is not formed, is determined by the condition: $p_{cr} = p_1 + at_{cr}$. Hence $t_{cr} = \frac{p_{cr} - p_1}{a}$. Then the mass of propellant burned at the range $[0, t_{cr}]$ is

DOI: 10.13009/EUCASS2017-105

$$M_1 = A\sigma\int_0^{t_{cr}} pdt = A\sigma(p_1 + 0.5at_{cr})t_{cr}$$

The mass of whole propellant (which was burned during the total time of operation)

$$M_p = A\sigma\int_0^{t_m} pdt = A\sigma(p_1 + 0.5at_m)t_m$$

Then the relative mass of propellant which was burned at the range when the slag was formed (i.e., at $t > t_{cr}$), is

$$m = 1 - \frac{\int_0^{t_{cr}} pdt}{\int_0^{t_m} pdt}$$

or

$$m = 1 - \frac{(p_1 + 0.5at_{cr})t_{cr}}{(p_1 + 0.5at_m)t_m}$$

where $t_m = \frac{p_2 - p_1}{a}$ is the total operating time of the gas generator; p_2 is the pressure at the end of the operation of the gas generator.
Substituting t_{cr} and t_m, one obtains

$$m = 1 - \frac{p_{cr}^2 - p_1^2}{p_2^2 - p_1^2}$$

This expression can be rewritten in the form

$$m = 1 - \frac{(p_{cr}/p_1)^2 - 1}{z^2 - 1} \tag{31}$$

where $z = p_2/p_1$ is the characteristic of the gas generator.

The mean pressure in the gas generator $p_m = \frac{1}{2}(p_2 + p_1)$. Thus $p_m/p_1 = \frac{z+1}{2}$ and $1/p_1 = \frac{z+1}{2p_m}$.

Substituting this expressions in (31), one obtains

$$m = 1 - \frac{(p_{cr}/p_m)^2\left((z+1)/2\right)^2 - 1}{z^2 - 1} \tag{32}$$

The calculation according to equation (32) corresponds only to those parameters for which $0 \le m \le 1$. In the case where the calculation by formula (32) gives negative values, it is necessary to put $m = 0$.
The relative mass of the slag

$$m_{slag} = m_r m \tag{33}$$

Figure 1 shows the dependence of $\frac{m_{slag}}{m_r}$ on p_m/p_{cr} at different $z = p_2/p_1$ for propellants A.

Let us consider the case of propellants B that satisfy the condition (25), when the slag is formed if the pressure in the combustion chamber less than the critical pressure (30).

DOI: 10.13009/EUCASS2017-105

In this case we similarly obtain

$$m = \frac{(p_{cr}/p_m)^2((z+1)/2)^2 - 1}{z^2 - 1} \tag{34}$$

Figure 2 shows the dependence of $\frac{m_{slag}}{m_r}$ on p_m/p_{cr} at different $z = p_2/p_1$ for propellants B.

It is necessary to note that the critical pressure, at which the formation of slag on the burning surface begins, is a property of only the propellant itself. However, the mean pressure in the gas generator, at which the formation of propellant residues in the gas generator begins, depends also on the ratio z. For this reason, in experiments, the mean pressure at which the accumulation of residues in the gas generator chamber begins, differs from p_{cr} and has a scatter related to the scatter of the diagram $p(t)$.

Note that when processing the real experimental data, we should use not a linear but a real experimental pressure diagram.

6. Conclusions

The model of the formation of residues in combustion of boron-containing propellants, developed in this work, allows explaining some regularities observed in experiments.

In this work, we do not into account the inverse effect of the conglomerates and slag, which form on the burning surface, on the burning rate of solid propellant, which can lead to a change in the nature of the agglomeration and slag formation.

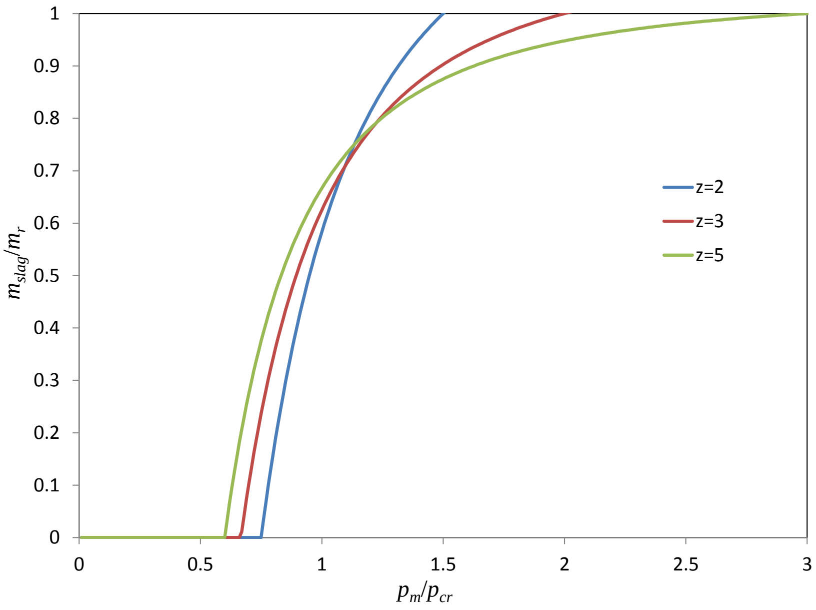

Figure 1: Dependence of $\frac{m_{slag}}{m_r}$ on p_m/p_{cr} at different $z = p_2/p_1$ for propellants A

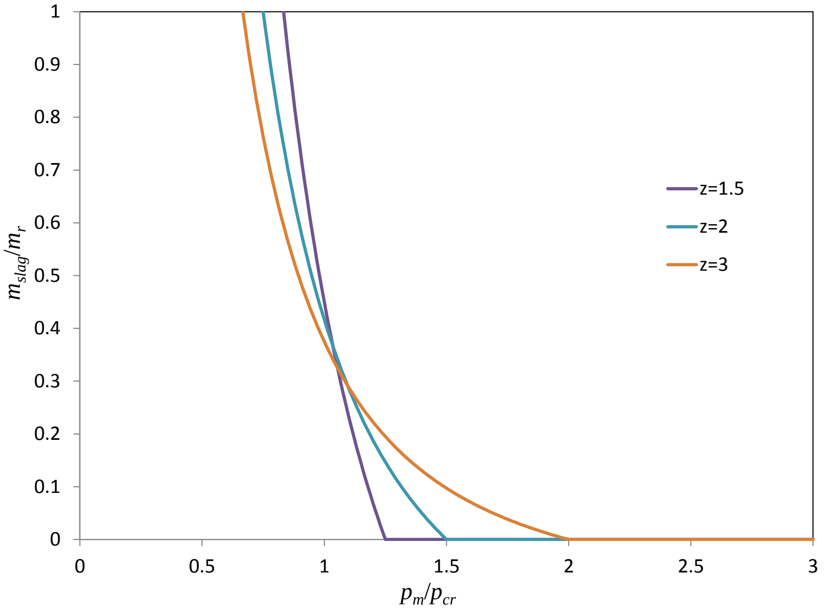

Figure 2: Dependence of $\frac{m_{slag}}{m_r}$ on p_m/p_{cr} at different $z = p_1/p_2$ for propellants B

References

[1] Vigot, C., L. Bardelle, and L. Nadaud. 1986. Improvement of Boron Combustion in a Solid-Fuel Ramrocket. In: *AIAA/ASME/SAE/ASEE 22nd Joint Propulsion Conference June 16-18, 1986/Huntsville, Alabama.*

[2] Vigot, C., A. Cochet, and C. Guin. 1991. Combustion Behavior of Boron-Based Solid Propellants in a Ducted Rocket. In: *Second International Symposium on Special Topics in Chemical Propulsion, "Combustion of Boron-Based Solid Propellants and Fuels", Lampoldshausen (FRG), March 4-6, 1991*

[3] Rashkovskii, S. A., Y. M. Milekhin, A. V. Fedorychev. 2016. Improving the completeness of combustion of boron particles in a solid-fuel ducted rocket owing to distributed air supply to the secondary combustor. *Doklady Physical Chemistry*. 471(2): 203-207.

[4] Gany, A. 1993. Combustion of Boron-Containing Fuels in Solid Fuel Ramjets. In: *Combustion of Boron-Based Solid Propellants and Solid Fuels (K.K. Kuo, R. Pein, Eds.), CRC Press, Boca Raton*.

[5] Rashkovskiy, S.A. 2017. Direct Numerical Simulation of Boron Particle Agglomeration in Combustion of Boron-Containing Solid Propellants. *Combust. Sci. Technol.* 189(8): 1277-1293.

[6] King, N.K. 1984. A Model of Boron Agglomerate Ignition. In: *Proc. of 21st JANNAF Combustion Meeting*.

[7] Laredo, D., and A. Gany. 1983. Combustion Phenomena Of Highly Metallized Solid Propellants, *Acta Astronautica.* 10(5-6): 437-441.

[8] Shevchuk, V. G., A. N. Zolotko, and D. I. Polishchuk. 1975. Ignition of packed boron particles. *Combust. Expl. Shock Waves.* 11(2): 189-192.

[9] DeLuca, L.T., E. Marchesi, M. Spreafico et al. 2010. Aggregation versus agglomeration in metallized solid rocket propellants. *Int J Energy Mater Chem Propuls* 9: 91-105.

[10] Liu, L.-L., G. Q. He, Y. H. Wang, and S. Q. Hu. 2015. Chemical Analysis of Primary Combustion Products of Boron-Based Fuel-Rich Propellant. *RSC Advances*. 5(123): 101416–101426.

[11] Liu, L.-L., G.-Q. He, Y.-H. Wang, S.-Q. Hu, and Y.-M. Liu. 2017. Factors Affecting the Primary Combustion Products of Boron-Based Fuel-Rich Propellants. *Journal of Propulsion and Power* 33(2): 333-337.

[12] Rashkovskiy, S.A. 2009. Direct numerical simulation of nano and conventional aluminum agglomeration in composite solid propellant combustion, *Int. J. Energetic Materials and Chemical Propulsion*, 8(1): 1-17.

[13] Pein, R., and S. Anders. 2000. Investigation of Fuel-rich Boron Combustion in a Pressurized Combustion Bomb. In: *The Fifth International Symposium on Special Topics in Chemical Propulsion, Combustion of Energetic Material.*, 33-34.

[14] Grigor'ev, V. G., K. P. Kutsenogii, and V. E. Zarko. 1981. Model of aluminum agglomeration during the combustion of a composite propellant. *Combust. Expl. Shock Waves*, 17(4): 356–362.

[15] Cohen, N.S. 1983. A Pocket model for aluminum agglomeration in composite propellants, *AIAA J.*, 21: 720-730.

[16] Kovalev, O. B., A. P. Petrov, and A. V. Fol’ts. 1987. Simulating aluminum powder aggregation in mixed condensed system combustion. *Combust. Expl. Shock Waves*, 23: 133–136.
[17] Gallier, S., and F. Hiernard. 2008. Microstructure of composite propellants using simulated packings and X-ray tomography. *J. Propulsion and Power* 24: 147-150.
[18] DeLuca, L.T., L. Galfetti, G. Colombo, F. Maggi, A. Bandera, V.A. Babuk, and V.P. Sindistkii. 2010. Microstructure Effects in Aluminized Solid Rocket Propellants. *AIAA Journal of Propulsion and Power* 26(4): 724-733.
[19] Rashkovsky, S.A. 1998. Metal Agglomeration in Solid Propellants Combustion: Part 1. Dynamical Model of Process. *Combust. Sci. Technol.* 139: 125-148.
[20] Rashkovsky, S.A. 1998. Metal Agglomeration in Solid Propellants Combustion: Part 2. Numerical Experiments. *Combust. Sci. Technol.* 139:.149-169.
[21] Rashkovskii, S. A. 2005. Statistical Simulation of Aluminum Agglomeration during Combustion of Heterogeneous Condensed Mixtures, *Combust. Expl. Shock Waves* 41:.174–184.
[22] Rashkovskii, S. A. 1999. Structure of heterogeneous condensed mixtures. *Combust. Expl. Shock Waves*, 35**(**5): 523–531.
[23] Rashkovskii, S. A. 2002. Role of the structure of heterogeneous condensed mixtures in the formation of agglomerates. *Combust. Expl. Shock Waves* 38**(**4): 435–445.
[24] Shyu, I-M., and T-K. Liu. 1995. Combustion Characteristics of GAP-Coated Boron Particles and the Fuel-Rich Solid Propellant. *Combust. Flame* 100: 634-644.