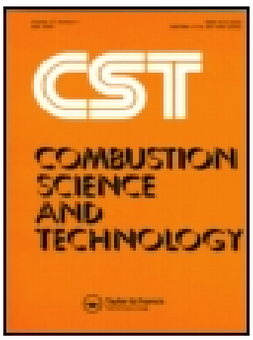

Taylor & Francis
Taylor & Francis Group

Combustion Science and Technology

ISSN: 0010-2202 (Print) 1563-521X (Online) Journal homepage: http://www.tandfonline.com/loi/gcst20

Direct Numerical Simulation of Boron Particle Agglomeration in Combustion of Boron-Containing Solid Propellants

Sergey A. Rashkovskiy

To cite this article: Sergey A. Rashkovskiy (2017) Direct Numerical Simulation of Boron Particle Agglomeration in Combustion of Boron-Containing Solid Propellants, Combustion Science and Technology, 189:8, 1277-1293, DOI: 10.1080/00102202.2017.1294586

To link to this article: http://dx.doi.org/10.1080/00102202.2017.1294586

COMBUSTION SCIENCE AND TECHNOLOGY
2017, VOL. 189, NO. 8, 1277–1293
http://dx.doi.org/10.1080/00102202.2017.1294586

Taylor & Francis
Taylor & Francis Group

Direct Numerical Simulation of Boron Particle Agglomeration in Combustion of Boron-Containing Solid Propellants

Sergey A. Rashkovskiy

Institute for Problems in Mechanics of the Russian Academy of Sciences, Moscow, Russia; Tomsk State University, Tomsk, Russia

ABSTRACT

The available experimental data on boron particles agglomeration during combustion of boron-containing solid propellants and a mechanism of the boron particles agglomeration are discussed. The model and the method of direct numerical simulation of the boron particles agglomeration have been suggested and developed. The calculation consists of two stages: the first stage is a simulation of a heterogeneous structure of solid propellant; the second stage is a calculation of a behavior of each boron particle, taking into account its interaction with other particles and with flow of gaseous combustion products of solid propellant. A mechanism of the adhesive bonds between the boron particles is suggested and the criterion of conglomerate detachment from the burning surface has been determined. The dependence of the strength of the adhesive bonds between the boron particles on the propellant burning rate and pressure is analyzed. The calculations of the boron particles agglomeration, which demonstrates the effect of the strength of adhesive bonds between boron particles on the intensity of agglomeration, have been carried out.

ARTICLE HISTORY
Received 13 April 2016
Revised 18 December 2016
Accepted 9 February 2017

KEYWORDS
Boron-containing solid propellant; Boron particles agglomeration; Combustion efficiency; Ducted rocket

Introduction

Boron-containing solid propellants with an oxidizer deficit and a high content (more than 30% by weight) of boron are considered to be promising propellants for ducted rockets (Gany, 1993; Kubota, 2007). Such solid propellants are capable of self-sustained combustion and their combustion occurs in a special gas generator. The temperature of the combustion products in the chamber of the gas generator is typically less than 2000 K. At this temperature, the boron particles are in a solid state (boron melting point ~2300 K), and practically do not 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 occurs in the oxygen of air; combustion products formed here flow out of the rocket nozzle into the environment, creating a thrust. Most parts of the energy, which is used for creation of the thrust, is released during the combustion of the boron particles in air flow in the secondary

CONTACT Sergey Rashkovskiy rash@ipmnet.ru Institute for Problems in Mechanics of the Russian Academy of Sciences, Vernadskogo Ave., 101/1, Moscow 119526, Russia.

Supplemental data for this article can be accessed on the publisher's website.

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. Keeping this in mind, the design of the ducted rocket is directed to obtain a maximum efficiency of boron combustion.

For theoretical estimation of the completeness of boron combustion in the 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 single boron particles do not leave the propellant burning surface but the large conglomerates (aggregates) containing a large number of the primary boron particles do. Accordingly, the combustion products of the solid propellant entering the secondary combustor contain not the single boron particles but their conglomerates. Note that hereinafter, the term "conglomerate" will be used 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 a solid propellant. This highlights a fundamental difference in the structure of the boron particles conglomerates and aluminum particles agglomerates (see below).

Particle size interferometry measurements resulted in a majority of recorded particle sizes falling at the range of 20–200 μm diameter (King, 1984). This is larger than anticipated and considerably larger than the virgin boron particle sizes of 1–2 μm.

Laredo and Gany (1983) studied the surface phenomenon associated with the combustion of boron-rich (40–50% of boron) solid propellants by means of high-speed photography using a windowed frame burner strand. They found out that propellants, containing boron additives in the range of 40–50% show irregular burning with some periodic phenomenon concerning the regression rate, agglomeration, and ejection of unburned propellant layers. They observed the increase of conglomerates' size at pressure above 50 bar.

Experiments (Vigot et al., 1986, 1991) 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 entering 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 (Vigot et al., 1986, 1991) indirectly indicate the presence of the boron particles conglomerates in combustion products of the boron-containing solid propellant. The combustion time of the boron particles conglomerate can significantly exceed the combustion time of single primary boron particle due to the difference in their sizes and due to the essential difference in the ignition and combustion behavior of the conglomerates as compared with a single boron particle. The experiments (Vigot et al., 1986, 1991) showed an ability to control the combustion time of the boron particles conglomerates due to optimization of a design of the secondary combustor.

Shevchuk et al. (1975) investigated experimentally 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. It was found that the ignition temperature of a conglomerate is substantially less than the ignition temperature of single boron particles (~1000 K vs. ~1900 K). The ignition model of the boron particles conglomerate

(Shevchuk et al., 1975), as well as the experimental data, show that conglomerate ignition temperature decreases with increasing the conglomerate specific reaction surface. The conglomerate specific reaction surface increases with increasing the conglomerate size and with decreasing the primary boron particle size in the conglomerate. Measurements (Shevchuk et al., 1975) showed that the conglomerate ignition temperature varies with their density monotonically and at a certain conglomerate density, the ignition temperature reaches a minimum. This is probably due to the blockage of pores in the conglomerate by the liquid boron oxide at decreasing the pores' size, which reduces the effective reaction surface of the conglomerate (Shevchuk et al., 1975). Decrease in the ignition temperature of the conglomerate as compared with that for a 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 longer as compared with that for a single boron particle, 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 an even more important role than the agglomeration of aluminum particles in conventional solid rocket motors. For those propellants that are actually used in the solid rocket motors, the agglomeration of aluminum particles practically does not affect the completeness of combustion, and reducing the effectiveness of solid rocket motors is connected mainly with the two-phase losses of specific impulse (~2–4%) and with an inertial deposition of heavy agglomerates in the combustion chamber, which increases the rocket motor passive weight. In ducted rockets, the incompleteness of boron combustion connected with a formation of conglomerates leads to significant additional (along with the two-phase losses) decreasing the specific impulse (down to 20%). In this regard, we believe that the fight against the boron particles agglomeration in combustion of boron-containing solid propellants in ducted rockets is an important and urgent problem.

One of the ways to increase the completeness of boron combustion is to increase the residence time of the combustion products in the secondary combustor due to increasing its length; however, this way leads to increasing the rocket weight and, consequently, to decreasing the efficiency of the propulsion system as a whole.

Another way to increase the completeness of boron combustion in ducted rockets is connected with decreasing the sizes of the conglomerates entering the secondary combustor from a gas generator. This method seems to be more promising.

Vigot et al. (1986, 1991) described some constructive ways to improve the boron combustion efficiency due to a special organization of the flow of solid propellant combustion products entering the secondary combustor. This is achieved due to dividing the flow of propellant combustion products at the exit of the nozzle of a gas generator onto several separate jets and their collision. In the collision of the supersonic jets, the conglomerates are subject to considerable overloads, which result in their crushing. The direct collisions of the conglomerates in counterflow jets also contribute to crushing the conglomerates. Vigot et al. (1986, 1991) have considered the various schemes of the jets collision and have shown that depending on the design of the nozzle, which creates the

jets, one can increase the combustion efficiency by 20–50% compared to the base variant in which the collision of the jets is absent.

Another way to reduce the size of the conglomerates entering the secondary combustor from the gas generator is reducing the intensity of the boron particles agglomeration on the burning surface of solid propellant, i.e., the elimination of the root, which causes the formation of large particles in the propellant combustion products. This can be achieved by optimizing the composition and structure of solid propellant, as well as using a variety of coatings of the boron particles, which reduce the tendency of the particles to agglomeration on the burning surface.

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

Moreover, for the correct calculation of the processes in the secondary combustor, it is necessary to know the exact combustion regularities of the conglomerates, rather than the single boron particles. In particular, for calculation of the ignition and combustion behavior of the conglomerate, one needs to know not only its size but also its structure and shape, which can significantly affect these processes.

Unfortunately, in the literature, there is very little experimental data on the boron particles agglomeration in combustion of the boron-containing solid propellants, while the theoretical works in this direction are absent in general. The goal of this work is to develop a model of the boron particles agglomeration in combustion of the boron-containing propellants, and to identify the factors that govern the process. The calculations performed using the developed model will demonstrate how the intensity of the boron particles agglomeration as well as the sizes and the shapes of the resulting conglomerates are changed with a change in the controlling factors.

Mechanism of boron particles agglomeration

The mechanism of boron particles agglomeration is largely similar to the mechanism of aluminum particles agglomeration in combustion of composite solid propellants (Rashkovskiy, 2009), but it has its own features. 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 decomposition of its components (binder, oxidizer particles, etc.) and simultaneously a heating of the boron particles occur. In contrast to aluminum particles in which the 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; 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 ($T_{m\mathrm{B_2O_3}} = 720\mathrm{K}$) is commensurable with a temperature of the propellant burning surface ($T_s = 700 - 1000\mathrm{K}$) and considerably less than a temperature of combustion products of the propellant in a gas generator ($T_b = 1500 - 2000\mathrm{K}$). This means that the boron particles on the propellant burning surface have the liquid oxide film. If two particles were in contact in the propellant, after their entry on the burning surface and melting their oxide films, they will be bound by the liquid bridge of

B_2O_3 and will be held together due to the surface tension of the liquid boron oxide. 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. Pein and Anders (2000) have shown that for hydroxyl-terminated polybutadiene (HTPB)-based solid propellants, a significant increase in B_4C content with increasing pressure is observed; at low pressures, there is a marked deviation from thermodynamic equilibrium, while at high pressures, the B_4C concentration approaches the equilibrium. The glycidyl azide polymer (GAP)-based propellants demonstrate the opposite behavior (Pein and Anders, 2000). For these propellants, the content of boron carbide in the combustion products decreases with increasing pressure. Results by Pein and Anders (2000) show that the boron carbide can be the 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.

As a result of all these processes, the single boron particles to not enter the propellant burning surface but the conglomerates of the boron particles do, which are connected by the relatively strong bonds; a certain force needs to be applied for breaking these bonds. Conglomerates form on the propellant burning surface in coral-like structures, which have different shapes, sizes, and porosity (Laredo and Gany, 1983). Gaseous combustion products generated due to 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 boron particles in the conglomerates, the breaking of the bonds occurs and the 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 (DeLuca et al., 2010) consisting of the molten aluminum and solid aluminum oxide, and formed due to merging the contacting primary aluminum particles after their melting, the boron particles conglomerates are the porous structures consisting essentially of the solid boron particles. The sizes of detached conglomerates, as well as their shapes, are random and determined by the propellant structure (concentration of powder components and their particle sizes) and the ration between the detached aerodynamic force and strength of the bonds between boron particles in conglomerate. The larger this ratio, the smaller the size of the conglomerates that leave the burning surface.

Thus, the structure of the propellant should be considered as a determining factor in the simulation of the boron particles agglomeration.

The mechanism of agglomeration, described above, imposes certain limitations on the methods of simulation of the boron particles agglomeration. For example, the pockets model (Cohen, 1983; DeLuca et al., 2010; Gallier and Hiernard, 2008; Grigor'ev et al., 1981; Kovalev et al., 1987) can be used in some cases for calculation of the aluminum

particles agglomeration, but is 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 (Rashkovsky, 1998a, 1998b; Rashkovskii, 2005) developed for the aluminum particles agglomeration and considering the process in dynamics can be used for calculation of the boron particles agglomeration. But in my opinion, the method of the direct numerical simulation of the agglomeration (Rashkovskiy, 2009) is more appropriate for this purpose. This method consists of modeling the solid propellant structure and the subsequent calculations of the behavior of each boron particle near the propellant burning surface, taking into account the changes in its thermal and chemical states and accounting for its mechanical interaction with the gaseous combustion products and with other boron particles.

In this article, the method of direct numerical simulation of agglomeration (Rashkovskiy, 2009) is developed as applied to boron-containing solid propellants.

In this method, the simulation of the agglomeration process consists of two stages: (i) modeling the propellant structure and (ii) the subsequent direct simulation of the boron particles agglomeration.

Simulation of the structure of boron-containing solid propellants

Calculation of a propellant structure is based on the "viscous suspension" method (Rashkovskii, 1999, 2002) and is as follows. The particles of all dispersed components (oxidizer, boron, etc.) are considered to be spherical and have the diameters D_i, where $i = 1, 2, \ldots$ is the particle number. For each kind of powder, its volume content in the propellant and the density distribution function of the sizes of corresponding particles is known. The calculation of propellant structure is conveniently carried out in nondimensional form. For this purpose a characteristic spatial scale is chosen, which is usually equal to a characteristic particle size. Nondimensional particle diameter is denoted as d_i. For a given size of a calculated propellant sample, the sets of the particles, which have the specified volume content in propellant, and a predetermined particles size distribution are generated by Monte Carlo method. After that, each particle is randomly placed into the computational domain. After such an arrangement, the particles can intersect, which does not correspond to the actual propellant structure. In order to create a system of disjoint particles, the "viscous suspension" algorithm is used, which reduced to the numerical solution of the set of the ordinary differential equations:

$$\frac{d\mathbf{r}_i}{dt} = \sum_{k \neq i} \frac{\mathbf{r}_i - \mathbf{r}_k}{|\mathbf{r}_i - \mathbf{r}_k|} \Delta_{ik} \tag{1}$$

$$\Delta_{ik} = \begin{cases} 1, & |\mathbf{r}_i - \mathbf{r}_k| < 0.5\,(d_i + d_k) \\ 0, & |\mathbf{r}_i - \mathbf{r}_k| \geq 0.5\,(d_i + d_k) \end{cases} \tag{2}$$

where $\mathbf{r}_i$ is the radius-vector of the center of the ith particle, d_i is the diameter of the ith particle, and t is the "time."

In this article, the periodic boundary conditions are used. The calculation ends when the system will not contain the overlapping particles.

From a physical point of view, the process of the particles placement, described by Eqs. (1) and (2), consists in the mutual "repulsion" of overlapping particles.

Calculations show that the process always converges to a structure in which there are no overlapping particles, if the particles volume fraction in the system is less than that for close packing. However, if the system contains the particles with substantially different sizes (diameters ratio greater than 7), the process of the particles placement slows down significantly.

In this case, the calculations can speed up by using the separate placement of the coarse and fine particles. For this purpose, the coarse particles are placed first. After the structure was found in which the intersecting coarse particles are absent, the placement of the fine particles at immobile coarse particles occurs. This method allows to significantly (several times) speed up the placement of particles with substantially different sizes.

The examples of calculation of the structure of the boron-containing propellant using the viscous suspension method are shown in Figure 1. In all of the examples, the same propellant composition is considered: boron, 17% vol.; AP, 27% vol.; the rest is a binder. The variants of calculations (Figure 1) are different only in the ratio of the sizes of the boron particles and ammonium perchlorate (AP) particles. Calculated samples contain up to 10^5 particles. In these examples, it is assumed that all of the particles of one kind have the same size (mono-disperse powders). Note that this assumption is not connected with a limitation of the viscous suspension method, which allows calculating the structures with any particle's size distribution.

Model of the boron particles agglomeration

For simulation of the boron particles agglomeration, the method similar to the "viscous suspension" method (Rashkovskii, 1999, 2002) will be used.

It is assumed that combustion of the propellant sample occurs in the direction opposite to the axis x. In this case the coordinate of the propellant burning surface at time t is:

$$x_f = L - ut \tag{3}$$

where L is the initial length of the propellant sample.

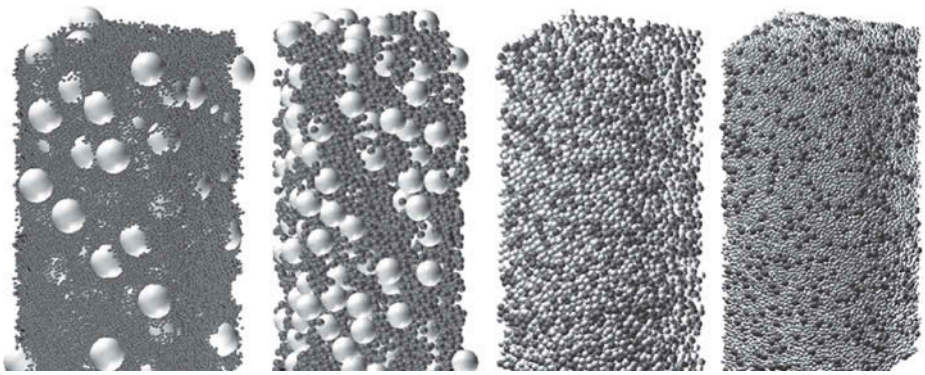

Figure 1. Characteristic structures of AP-based boron-containing solid propellants at different ratios of particle sizes of boron (D_B) and AP (D_{AP}). The volume fractions of the powder components in all samples are the same: boron, 17%; AP, 27%. The light particles are AP; the dark particles are boron. (a) D_B/D_{AP} = 0.1; (b) D_B/D_{AP} = 0.3; (c) D_B/D_{AP} = 1.0; (d) D_B/D_{AP} = 2.0.

In general, the propellant burning rate u as well as the boron particles conglomerate's size depend on the propellant structure. This means that changes in the composition and structure of the propellant will 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 the agglomeration process and the effect of the agglomeration process on the burning rate. In this article, a simplified approach is 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 a 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.

Let us consider the method of calculation of the boron particles agglomeration during combustion of a solid propellant.

The boron particles, which are under the burning surface (i.e., which have the coordinate $x < x_f$), are surrounded by the binder and are considered to be immobile. The boron particles, which are above the burning surface, can move, and they interact with each other and with the gaseous combustion products flowing from the burning surface. It is considered that the contacting boron particles are connected to each other by the adhesive forces, the nature of which was discussed above.

The strong bonds that connect the contacting boron particles can be broken under certain conditions.

Let us consider the motion of each boron particle above the burning surface taking into account all the forces acting on it. The motion of the boron particles above the burning surface is described by the system of the equations:

$$m_i \frac{d\mathbf{V}_i}{dt} = \sum_k \mathbf{F}_{ik} + \mathbf{f}_i \tag{4}$$

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{V} \tag{5}$$

where $\mathbf{r}_i = (x_i, y_i, z_i)$ are the coordinates of the center of ith particle, $\mathbf{V}_i$ is its velocity, $\mathbf{F}_{ik}$ is the force which acts on the particle i from the side of the particle k, $\mathbf{f}_i$ is the force acting on the ith particle from the side of gaseous combustion products flowing from the burning surface.

The system of Eqs. (4) and (5) is solved for all particles that are above the burning surface, i.e., for those particles for which:

$$x > x_f \tag{6}$$

At low Reynolds numbers, which corresponds to the flow above the burning surface, one can write approximately:

$$\mathbf{f}_i = \mu\,(\mathbf{U}_i - \mathbf{V}_i) \tag{7}$$

where $\mathbf{U}_i = (U_i, 0, 0)$; U_i is the velocity of the gaseous combustion products, flowing from the burning surface under ith boron particle (due to heterogeneity of the composite propellant, in different points of the burning surface and at different instants, the instantaneous burning rate and, hence, the velocity of gaseous combustion products will be different); μ is some coefficient ("aerodynamic drag" coefficient of the particle), which depends on the particle size, on its position in a conglomerate, on the shape and sizes of the conglomerate, on its porosity, on the composition and the temperature of the gaseous combustion products surrounding the conglomerate, and so on. Moreover, we consider this coefficient to be constant. It can be considered as a matching coefficient of the model. For estimation of this coefficient, e.g., the Stokes' law can be used; in this case $\mu = 3\pi D\mu_g$, where D is the diameter of the original boron particle and μ_g is the dynamic viscosity of the gaseous combustion products near the burning surface.

The velocity of the gaseous combustion products flowing from the burning surface:

$$U_i = \eta_i (1 - m_B) \frac{\gamma}{\rho} u \tag{8}$$

where m_B is the mass fraction of boron in propellant; η_i is the factor that takes into account the heterogeneity of the propellant; γ is the propellant density; $\rho = \frac{p}{RT_{as}}$ is the density of gaseous combustion products; p is pressure; and T_{as} is a characteristic temperature of gaseous combustion products above the burning surface, e.g., $T_{as} = 0.5(T_s + T_b)$. In this article, we assume $\eta_i = 1$, then U_i is considered to be the mean (on the propellant burning surface) velocity of flow of gaseous combustion products:

$$U = (1 - m_B) \frac{\gamma}{\rho} u \tag{9}$$

The adhesive force between contacting particles prevents their detachment and plays a role of "elastic bond" between the particles. Consequently, this force can be considered linearly dependent on deformations in the contact area of the particles. Then, for the force of interaction of the particles, one can write:

$$\mathbf{F}_{ik} = K_{ik} \frac{\mathbf{r}_k - \mathbf{r}_i}{|\mathbf{r}_k - \mathbf{r}_i|} \left(|\mathbf{r}_k - \mathbf{r}_i| - \frac{1}{2}(D_i + D_k) \right) \tag{10}$$

where K_{ik} is the factor characterizing the rigidity of the bonds between contacting particles i and k; D_i is the diameter of ith original boron 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.

Taking into account that the dissipative (viscous) forces acting on the particle are substantially greater than the inertial forces, one can neglect the left-hand side in Eq. (4). Then taking into account Eqs. (5), (7), and (10), one obtains:

$$\frac{d\mathbf{r}_i}{dt} = \frac{K}{\mu} \sum_k \frac{\mathbf{r}_k - \mathbf{r}_i}{|\mathbf{r}_k - \mathbf{r}_i|} \left(|\mathbf{r}_k - \mathbf{r}_i| - \frac{1}{2}(D_i + D_k) \right) + \mathbf{U}_i \tag{11}$$

The system (11) is a so-called "overdamped approximation" of Eqs. (4), (5), (7), and (10).

This system of equations allows to calculate the movement of all boron particles above the burning surface of a solid propellant. At the positive values, the force (10) is a tearing

one. Each bond has a tensile strength F_{ik}^0: if the tearing force (10) exceeds the tensile strength, the breaking of the bond between the particles i and k occurs, and this particle 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 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 of 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.

Thus, if the condition:

$$\frac{(\mathbf{r}_k - \mathbf{r}_i)\mathbf{F}_{ik}}{|\mathbf{r}_k - \mathbf{r}_i|} > F^0 \tag{12}$$

is satisfied at some instant, then hereinafter the particles i and k are considered to not be in contact, and there will be no interaction between them: $\mathbf{F}_{ik} = 0$.

The condition of the breaking of the bonds (12) with taking into account (10) can be rewritten as:

$$|\mathbf{r}_k - \mathbf{r}_i| > \frac{1}{2}(D_i + D_k) + F^0/K \tag{13}$$

Let us proceed to nondimensional variables, keeping for $\mathbf{U}$, $\mathbf{r}_k$, and t the previous notations. We choose the characteristic size of the original 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 original boron particle is $d = D/D_0$. As follows from (9), the nondimensional velocity of the gaseous combustion products near the burning surface is obtained:

$$\mathbf{U} = ((1 - m_B)\gamma/\rho, 0, 0) \tag{14}$$

In nondimensional variables, the velocity of movement of the propellant burning surface (the burning rate) is equal to unity, so the movement of the burning surface is described by the equation:

$$x_f = L - t \tag{15}$$

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

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{U}_i + \varepsilon \sum_k \xi_{ik} \frac{\mathbf{r}_k - \mathbf{r}_i}{|\mathbf{r}_k - \mathbf{r}_i|} \left(|\mathbf{r}_k - \mathbf{r}_i| - \frac{1}{2}(d_i + d_k) \right) \tag{16}$$

where $\xi_{ik} = 0$ if the condition:

$$|\mathbf{r}_k - \mathbf{r}_i| > \frac{1}{2}(d_i + d_k) + \delta \tag{17}$$

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 $\xi_{ik} = 1$. 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 $\xi_{ik} = 1$ until the condition (17) will satisfy.

This allows taking into account the emergence of new adhesive bonds between boron particles in the course of their movement:

$$\varepsilon = \frac{KD_0}{\mu u} \tag{18}$$

$$\delta = \frac{F^0}{KD_0} \tag{19}$$

The parameter ε is the nondimensional rigidity of the bond, and the parameter δ is the nondimensional maximum allowable deformation of the bond at which its destruction (breaking) occurs.

Besides the parameters characterizing the propellant structure (content and dispersity of the components), the model (16)–(19) 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 (9) is considered to be well 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 be described by the power law:

$$u = u_0(p/p_0)^{\nu} \tag{20}$$

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

Then one can write:

$$\varepsilon = \varepsilon_0(p/p_0)^{-\nu} \tag{21}$$

$$U = U_0(p/p_0)^{-1} \tag{22}$$

where

$$\varepsilon = \frac{KD_0}{\mu u_0} \tag{23}$$

$$U_0 = (1 - m_B)\frac{\gamma}{\rho_0}u \tag{24}$$

$$\rho_0 = \frac{p_0}{RT_{as}} \tag{25}$$

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 condensed phase of propellant $\tau = \kappa/u^2$ (where κ is the thermal diffusivity of the condensed phase of propellant); the longer the boron particles are in the 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 condensed phase can be described by the power function. In this case one obtains:

$$\delta = Au^{-2\alpha} \tag{26}$$

where A and $\alpha > 0$ are the constants.

Then one can write:

$$\delta = \delta_0 (p/p_0)^{-2\alpha\nu} \tag{27}$$

where

$$\delta_0 = Au_0^{-2\alpha} \tag{28}$$

is the constant.

If the dependencies of the parameters K, μ, F^0, and T_{as} on pressure are weak, then the expressions (21), (22), and (27) 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, Shyu and Liu (1995) covered the micron-size boron particles (average particles diameter ~51 μm) with glycidyl azide polymer (GAP) and investigated their combustion in a hot gas flow of a flat-flame burner and in composite solid propellant. The results by Shyu and Liu (1995) show that propellants containing the amorphous boron particles coated with GAP, demonstrate a higher burning rate and a lower intensity of agglomeration as compared with the base composition containing the uncoated boron particles.

Using the Stokes' law, one can estimate the aerodynamic force that acts on the single boron particle: $F_{a1} = 3\pi D\mu_g U$. Assuming $D = 3{\cdot}10^{-6}$ m; $\mu_g = 3{\cdot}10^{-5}$ kg/(m·s); and U=10 m/s one obtains $F_{a1} \sim 10^{-8}$ N. The bonding force between two contacting boron particles connected with surface tension has an order $F_{ad1} \sim \sigma D$, where σ is the surface tension of the molten boron oxide that forms a film on the surface of the boron particle. Assuming σ = 100 mJ/m^2 one obtains $F_{ad1} \sim 3{\cdot}10^{-7}$ N. It is necessary to take into account that the rupture of the conglomerate and its detachment from the propellant burning surface is the collective effect in which many original boron particles participate.

Obviously, an intense agglomeration is possible only if the coefficient ε satisfies the condition:

$$\varepsilon\delta > U \tag{29}$$

Otherwise, the single boron particles will leave the burning surface and agglomeration will not occur.

Using (21), (22), and (27), one can rewrite the condition (29) in the form:

$$\varepsilon_0 \delta_0 (p/p_0)^{-(1+2\alpha)\nu} > U_0 (p/p_0)^{-1} \tag{30}$$

From this inequality, it follows that two different kinds of propellants are possible:
(a) The propellants which have:

$$(1+2\alpha)\nu < 1 \tag{31}$$

For example, for $\alpha = 1$ this corresponds to $\nu < 0.33$.
In this case, the condition (30) takes the form:

$$(p/p_0)^{1-(1+2\alpha)\nu} > \frac{U_0}{\varepsilon_0 \delta_0} \tag{32}$$

It follows that there is a threshold pressure p_a:

$$p_a/p_0 = \left(\frac{U_0}{\varepsilon_0 \delta_0}\right)^{\frac{1}{1-(1+2\alpha)\nu}} \tag{33}$$

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 have

$$(1+2\alpha)\nu > 1 \tag{34}$$

For example, for $\alpha = 1$ this corresponds to $\nu > 0.33$.
In this case the condition (30) takes the form:

$$(p/p_0)^{(1+2\alpha)\nu-1} < \frac{\varepsilon_0 \delta_0}{U_0} \tag{35}$$

It follows that there is a threshold pressure p_b:

$$p_b/p_0 = \left(\frac{\varepsilon_0 \delta_0}{U_0}\right)^{\frac{1}{(1+2\alpha)\nu-1}} \tag{36}$$

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 kinds of boron-containing propellants, depending on their composition, which are different by a behavior of the boron 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. For example, according to Vigot et al. (1986, 1991), the combustion efficiency in the secondary combustor increases significantly with increasing pressure in the combustion chamber of the gas generator with other conditions being equal. This can occur due to an increase of the temperature of the propellant combustion products with increasing pressure; however, it is more likely that the observed increase in combustion efficiency (over 20%) is associated with a reduction of the degree of the boron particles agglomeration with increasing pressure. Laredo and Gany (1983), on the contrary, observed a significant increase in the boron particles agglomeration for $p > 50$ atm. Unfortunately, Laredo and Gany (1983) and Vigot et al. (1986, 1991) have not indicated the values of the pressure exponent ν for the used propellants, which does not allow checking the criterion (30).

Note that relations (21), (22), and (27) can be rewritten as:

$$\varepsilon = \varepsilon_*(p/p_*)^{-\nu} \tag{37}$$

$$U = (p/p_*)^{-1} \tag{38}$$

$$\delta = \delta_*(p/p_*)^{-2\alpha\nu} \tag{39}$$

where

$$p_* = U_0 p_0 \tag{40}$$

$$\varepsilon_* = \varepsilon_0 U_0^{-\nu} \tag{41}$$

$$\delta_* = \delta_0 U_0^{-2\alpha\nu} \tag{42}$$

Illustration of the model

The calculation was made as follows. The simulation of the structure of the selected propellant was carried out. After that, on each time step Δt, the movement of the burning surface by a distance Δt (in nondimensional variables) occurred and the calculation of the movement of all boron particles above the propellant burning surface was performed according to Eq. (16) taking into account the conditions of breaking the bonds between the particles (17). In solving Eq. (16), the periodic boundary conditions in y and z directions were used, which allowed eliminating the influence of the transverse sizes of the calculated sample on the size of the conglomerates.

The time step was chosen from the condition:

$$\Delta t << \delta/U \tag{43}$$

which provides the stability of the calculation.

The program of visualization of the results of calculation allowed presenting them as the movies, which clearly demonstrate the process of the boron particles agglomeration. The movies demonstrating the described results are provided in the Supplemental Material (available online).

From a practical point of view, the impact of the parameter δ, which characterizes the strength of the adhesive bonds between the boron particles in the conglomerate to the intensity of agglomeration, is of particular interest. According to (26), this parameter can be reduced at a constant pressure due to the increase in the burning rate (for example, by introducing catalysts into the propellant) as well as by applying a coating on the boron particles, which reduces the adhesion between the particles (Shyu and Liu, 1995).

Figure 2 shows the typical frames of the combustion of boron-containing propellant obtained in calculations with different values of the parameter δ for propellant structure shown in Figure 1b. The values $\varepsilon = 2.4 \times 10^5$ and $U = 109$ were used in the calculations, which for $m_B = 0.3$ corresponds to pressure $p \approx 30$ atm.

In calculations, it was assumed that the AP particles burn out on the burning surface of solid propellant.

The results of calculations demonstrate a significant increase in the boron particles agglomeration with an increase in the strength of adhesive bonds between particles (i.e.,

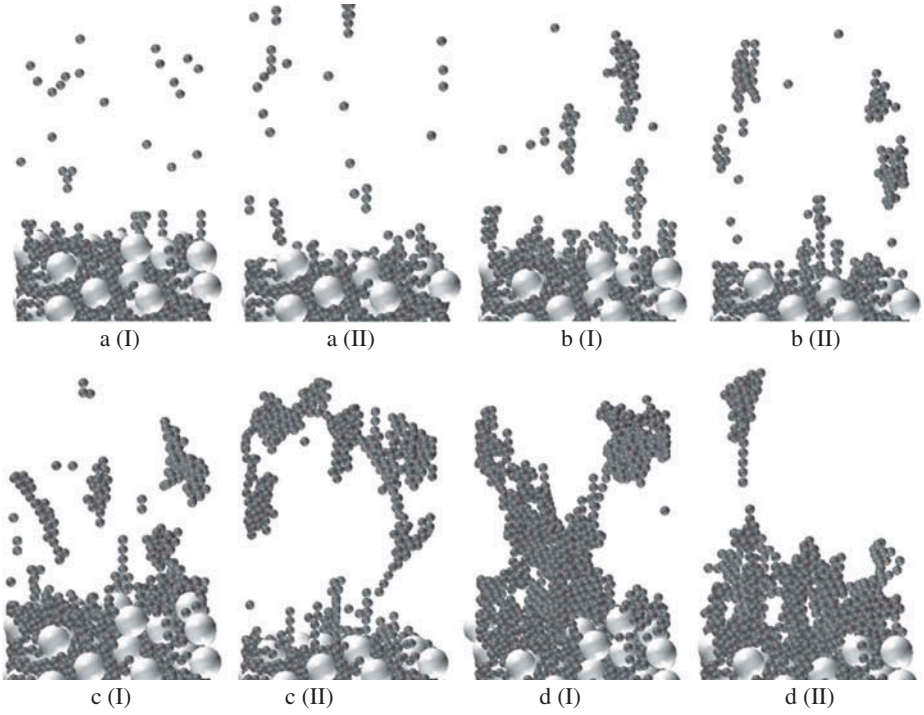

Figure 2. Visualization of the results of calculations of the boron particle agglomeration for propellant variant shown in Figure 1b, for different values of the parameter δ: (a) $\delta = 0.01$; (b) $\delta = 0.025$; (c) $\delta = 0.05$; (d) $\delta = 0.1$. The variants I and II correspond to different time moments for the same values of parameter δ.

with an increase in parameter δ) when all other parameters remain unchanged. Thus, at $\delta \leq 0.01$, the boron particles agglomeration is practically absent (Figure 2a) and the single boron particles that are in the propellant leave the burning surface. At the same time, at $\delta \geq 0.1$, a thick carcass layer, which consists of the sintered boron particles, is formed on the propellant burning surface. This layer is periodically detached from the burning surface under action of the gaseous combustion products of the propellant. This is in full compliance with the available experimental data and with the qualitative analysis given above.

The calculations show that the boron particles conglomerates have a random and irregular shape and cannot even be considered as the spherical particles. This fact should be taken into account in the models of ignition and combustion of the boron particles conglomerates in the secondary combustor of the ducted rockets.

Conclusion

The model and the common method of calculation of the boron particles agglomeration during combustion of the boron-containing solid propellants have been 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 the aerodynamic

detached force from the side of the flow of gaseous combustion products of solid propellant. The mechanism of formation of the adhesive bonds between the boron particles and a dependence of the strength of these bonds on the residence time of boron particles in the heated layer of condensed phase of propellant have been suggested. The most probable causes of the adhesive bonds between the boron particles are the surface tension in the liquid boron oxide and a formation of refractory compounds (boron carbide and boron nitride) near the burning surface. The criterion of occurrence of intense boron particles agglomeration has been suggested, and it was shown that depending on the propellant burning rate law, two different kinds of propellants with different behavior of the agglomeration process at pressure change can exist. The proposed model and calculation method admit further developing due to taking into account the various effects and processes, which accompany the combustion of solid propellants and the boron particles agglomeration. In particular, the proposed model can be supplemented by the equations describing the thermal and chemical interaction of each individual boron particle with other particles and with the products of decomposition of solid propellant (both liquid and gaseous) since the release of the boron particle on the burning surface. This allows describing the non-uniform thermal state of the conglomerate and its chemical composition at all stages of the conglomerate formation and evolution, and taking into account the thermal and chemical heterogeneity of conglomerate in calculation of parameters δ and U_0 for each pair of contacting boron particles. Also, within the framework of this model, it is possible to take into account the effect of gravity and flight accelerations on the boron particles agglomeration. These issues are expected to be considered in future papers.

Funding

Funding was provided by the Tomsk State University competitiveness improvement program.

ORCID

Sergey A. Rashkovskiy http://orcid.org/0000-0001-5683-5988

References

Cohen, N.S. 1983. A pocket model for aluminum agglomeration in composite propellants. *AIAA J.*, **21**, 720–730.

DeLuca, L.T., Galfetti, L., Colombo, G., Maggi, F., Bandera, A., Babuk, V.A., and Sindistkii, V.P. 2010. Microstructure effects in aluminized solid rocket propellants. *J. Propul. Power*, **26**(4), 724–733.

Gallier, S., and Hiernard, F. 2008. Microstructure of composite propellants using simulated packings and X-ray tomography. *J. Propul. Power*, **24**, 147–150.

Gany, A. 1993. Combustion of boron-containing fuels in solid fuel ramjets. In: K.K. Kuo, and R. Pein (Eds.), *Combustion of Boron-Based Solid Propellants and Solid Fuels*, CRC Press, Boca Raton, FL.

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

King, N.K. 1984. A model of boron agglomerate ignition. Presented at the 21st JANNAF Combustion Meeting, The Johns Hopkins University, Applied Physics Laboratory, Laurel, MD, October 1–4

Kovalev, O.B., Petrov, A.P., and Fol'ts, A.V. 1987. Simulating aluminum powder aggregation in mixed condensed system combustion. *Combust. Explos. Shock Waves*, **23**, 133–136.

Kubota, N. 2007. *Propellants and Explosives Thermochemical Aspects of Combustion*, Second Completely Revised and Extended Edition, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 439–468.

Laredo, D., and Gany, A. 1983. Combustion phenomena of highly metallized solid propellants. *Acta Astronaut.*, **10**(5–6), 437–441.

Pein, R., and Anders, S. 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 Materials*, Stresa (Lake Maggiore), Italy, June 18–22; pp. 33–34.

Rashkovsky, S.A. 1998a. Metal agglomeration in solid propellants combustion: Part 1. Dynamical model of process. *Combust. Sci. Technol.*, **139**, 125–148.

Rashkovsky, S.A. 1998b. Metal agglomeration in solid propellants combustion: Part 2. Numerical experiments. *Combust. Sci. Technol.*, **139**, 149–169.

Rashkovskii, S.A. 1999. Structure of heterogeneous condensed mixtures. *Combust. Explos. Shock Waves*, **35**(5), 523–531.

Rashkovskii, S.A. 2002. Role of the structure of heterogeneous condensed mixtures in the formation of agglomerates. *Combust. Explos. Shock Waves*, **38**(4), 435–445.

Rashkovskii, S.A. 2005. Statistical simulation of aluminum agglomeration during combustion of heterogeneous condensed mixtures. *Combust. Explos. Shock Waves*, **41**, 174–184.

Rashkovskiy, S.A. 2009. Direct numerical simulation of nano and conventional aluminum agglomeration in composite solid propellant combustion. *Int. J. Energetic Mater. Chem. Propul.*, **8**(1), 1–17.

Shevchuk, V.G., Zolotko, A.N., and Polishchuk, D.I. 1975. Ignition of packed boron particles. *Combust. Explos. Shock Waves*, **11**(2), 189–192.

Shyu, I.-M., and Liu, T.-K. 1995. Combustion characteristics of GAP-coated boron particles and the fuel-rich solid propellant. *J. Combust. Flame*, **100**, 634–644.

Vigot, C., Bardelle, L., and Nadaud, L. 1986. Improvement of boron combustion in a solid-fuel ramrocket. Presented at the AIAA/ASME/SAE/ASEE 22nd Joint Propulsion Conference, Huntsville, AL, June 16–18.

Vigot, C., Cochet, A., and Guin, C. 1991. Combustion behavior of boron-based solid propellants in a ducted rocket. Presented at the Second International Symposium on Special Topics in Chemical Propulsion, "Combustion of Boron-Based Solid Propellants and Fuels," Lampoldshausen (FRG), March 4–6.