Analysis and Synthesis of Solutions for the Agglomeration Process Modeling

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Abstract

The present work is devoted development of model of agglomerating process for propellants based on ammonium perchlorate (AP), ammonium dinitramide (ADN), HMX, inactive binder and nanoaluminum. Generalization of experimental data, development of a physical picture of agglomeration for listed propellants, development and analysis of mathematical models are carried out. Synthesis of models of various phenomena taking place at agglomeration implementation allows predicting of size and quantity, chemical composition, structure of forming agglomerates and its fraction in set of condensed combustion products. Obtained results correspond to available experimental data. It is supposed that analogical method based on analysis of mathematical models of particular phenomena and their synthesis will allow implementing of the agglomerating process modeling for other types of metalized solid propellants.

1. Introduction

Usage of metal fuel (aluminum) in propellant composition has a consequence formation of condensed combustion products. As a rule the set of condensed products includes two fractions. The first one consist of smoke oxide particles (SOP) having size typically no more than 1 μm. The second one includes set of agglomerates formed due to condensed products enlargement processes in surface layer of burning propellant. Agglomerates could exceed initial metal particles sizes in 10 – 1000 times (agglomerates more than 1 mm in diameter are experimentally obtained [1]).

The presence of agglomerates in set of combustion products results in appearance of problems associated with efficiency of rocket motor working. These include slag accumulation, two-phase and chemical losses of specific impulse, erosion of thermal protection, increased heat stress on the elements of rocket motor. In should be noted that there are experimental data of positive effect of agglomerating process on the propellant burning law [2].

Commonly, the data of size of condensed particles is used only at calculations of two-phase flows and this influence on work of rocket motor. However, in several papers (for example [3]) it is concluded that information about the chemical composition and structure of condensed particles is necessary. The value of unoxidized aluminum in the composition of depositing agglomerates is important information for description of interaction between two-phase flows and ablative materials [4]. Structure of agglomerates and especially presence of gaseous cavities has significant influence on particles behavior in the gaseous flows [5]. Thus, knowledge of amount of agglomerates in the set of combustion products, chemical composition and structure of agglomerates is necessary besides of sizes agglomerates for the description of agglomeration process and its influence on the “propellant – rocket motor” quality. Adequate prediction assumes necessity of consideration of all set of the phenomena at realization agglomeration process.

In previous papers different methods for the agglomeration process modeling are presented. Models presented in [6, 7] ensure prediction of the enlargement degree depending on *residence time* of the agglomerating particle on the surface of burning propellant. According to the paper [6] residence time is constrained by the moment of metal particle ignition. This statement contradicts the experimental data [8]: metal ignition is not necessarily condition for the breaking away of agglomerating particles.

In [7] residence time value depends on the relation between the forces acting on the particle. It is assumed that preventing of breaking away force is provided by the sintering of initial metal particles. Determination of

applicability limits of this model is hindered by the absence of comparison of the results of its parametric analysis with experimental data on variation of propellant composition and combustion conditions.

Another method presented in papers [9, 10] is based on the idea of significant influence of propellant structure on the degree of particle agglomeration. The concept of "*pockets*" is used. This notion is associated with a spatial area bounded by several oxidizer particles. Formation of the agglomerates occurs only within "pockets". Such method allowed to explain the experimentally fixed dependence of size agglomerates on size of oxidizer particles and its quantities. However some statements used in some cases does not correspond to the experimental data. First, the "pocket" mechanism of agglomeration is not universal. Second, not all oxidizer particles are involved in formation of the "pockets".

Model of the agglomeration process presented in [11, 12] is based on the statistical modeling. According to the author's opinion the model takes into account all of phenomena and can be used for wide range of metalized solid propellants. However, some of basic statements contradict the experimentally fixed phenomena. First of all, consideration of a *skeleton layer* formation at propellant burning which provide the condensed products coalescence is absent. In author's opinion formation of connected particles structures is necessary for the agglomeration process. These structures during propellant combustion form subagglomerates – molten condensed substances. Subaglomerates are moving onto the surface of burning propellant and merge among themselves and with agglomerating particles located on the surface. According to experimental data [2, 14] connections between initial metal particles at nanoaluminum usage significantly influence on agglomerating process, but it is <u>not</u> necessary condition for possibility of the agglomeration process realization. Absent of consideration of skeleton layer does not allow to understand the origins of forces that restraint molten particles on the surface of burning propellant as well as ensure their movement and merging within surface layer.

Important result of works [8, 13] was consideration of conception of the *skeleton layer*. The skeleton layer (SL) is a gas-permeable three-dimensional structure consisting mainly of the metal and its oxide, as well as thermo-stable carbonic elements, and comprising the top portion of surface layer. Presence of the SL ensures long-time residence, movement, merging and enlargement of high-temperature agglomerating particle in the surface layer of burning propellant. Forming of the SL is necessary condition for realization of the agglomeration process. Depending on the SL properties propellants were divided into two classes – **A** and **B**.

The model presented in paper [15] allows predicting of function of size distribution of agglomerates at burning of propellants of class **A** (in terms of works [8, 13, 14]). Consideration within the framework of model of conditions of particle position on the surface and particle breaking away is very important. It allowed modeling of size of agglomerates forming by the "pocket" and "interpocket" agglomeration mechanisms. Results of analysis of the model reproduce experimentally fixed regularities.

As a whole it is possible to confirm that available by this time models are limited by the determination of agglomerate size only, that seems to be not enough. The main difference of the model presented in this paper is possibility determining besides the quantity and size of agglomerates also parameters of chemical composition and structure.

Variety of displays of the agglomeration makes illusive development of universal model which would take into account all features of the agglomeration process at combustion of different types of propellants in various conditions. However the problem can be solved for specific types of propellant.

The present work is devoted development of model of agglomerating process for propellants based on ammonium perchlorate (AP), ammonium dinitramide (ADN), HMX, inactive binder and nanoaluminum. These propellants belong to the propellants of class **A** and have similar regularities of agglomeration process [14]. It should be noted that attractive feature of these propellants is possibility to obtain favorable dependence of propellant burning rate on pressure [2].

2. Physical picture of the agglomeration process

Physical picture of the agglomeration process at burning of considered propellants is formulated on the basis of available by this time experimental data analysis. The experiments were performed with use of following techniques [1, 8, 13, 14, 18]:

- quench-collection of condensed combustion products at combustion of propellant samples and subsequent chemical and structural analysis propellant at a variation of parameters of propellant composition, pressure, value and direction of accelerative forces;
- investigations of combustion residues or quenching products;
- visualization of the surface of burning propellant.

The first method allows obtaining quantitative data of size, chemical composition and structure of agglomerates. Most important of them are:

- $f_m\ (D)$ – mass function of size distribution density of agglomerates;

- Z_m – fraction of unburned metal in agglomerates relative to initial metal in propellant;
- Z_m^{ox} – fraction of initial metal in propellant used to form oxide in agglomerates;
- Z_m^{a} – fraction of initial metal in propellant used to form agglomerates;
- η – mass fraction of oxide in agglomerate;
- D_{43} – mass-medium diameter of agglomerates, μm.

Both the other methods provide obtaining qualitative information describing agglomerating particles behavior on the surface of burning propellant and in the near-surface zone of gas phase.

Analysis of experimental data allowed to indicate following stages of agglomeration process.

2.1 Formation of the skeleton layer

Forming of the SL is necessary condition for the agglomeration process realization. Presence of the SL provides possibility of long-time residence and enlargement by merging among themselves of high-temperature agglomerating particles within and on the surface of SL [7, 8, 13, 14].

Possibility of the SL formation is connected with conditions of the binder decomposition – first of all with oxidizing components concentration. Formation of the SL for considered propellants occurs only within the *"pockets"*. (Figure 1). Within other structural formations – *"interpocket bridges"* which are characterized by increased oxidizing components concentration – formation of the SL is not occur. It should be noted that usage of active binders leads to increase of oxidizing components as well as within the "pockets" which in turn leads to suppression of the agglomeration process [14].

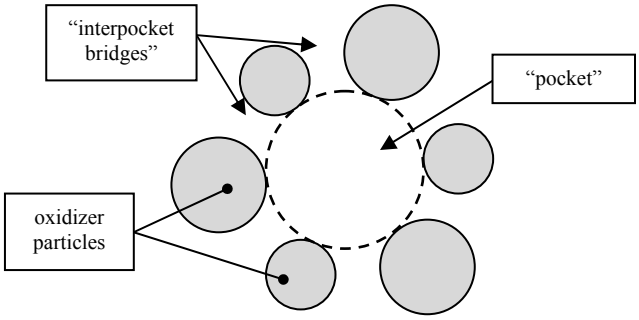

Figure 1: The local area of propellant containing a "pocket"

Thus, formation of the SL for considered propellants is connected with presence of the "pockets". Therefore for such propellants there is the dependence between fraction of agglomerates (parameter Z_m^{a}) and propellant structure.

2.2 Ignition and burning of metal

The combustion of considered propellants corresponds to regularities of the class **A** propellants burning [14], thus the temperature of metal ignition does not exceed the decomposition temperature of thermo-stable carbonic elements of the SL. Gas-permeability of the SL structure ensures the access for oxidizing components inside the SL. Presence of solid oxide film does not preclude ignition, since oxidizing gases are able to penetrate through the oxide film cracks.

After ignition of metal, oxide is melting relatively quickly. This ensures the possibility of spreading of liquid metal and oxide inside the SL. It is considered that existence of chemical interaction between these substances and carbon ensures the liquid metal and oxide wetting of carbonic elements. Therefore, these liquid substances fill the SL pores.

After ignition burning if metal occurs in the heterogeneous mode, and it is accompanied by accumulation of liquid oxide. This burning mode continues until the temperature of the metal particles reaches the value required for the heterogeneous mode is transferring to the gas-phase mode. At the same time accumulation of liquid oxide is terminated, and product of combustion of metal in this mode is the SOP carried away by the gas flow [8, 13].

2.3 Formation of individual agglomerating particles

During combustion of the "pocket" liquid metal and oxide are moving up to the surface of SL and forming the particle staying at the I equilibrium state (Figure 2). At this state breaking away of the particle is not possible due to high level of adhesion between particles substance and elements of the SL [15]. As the "pocket" burns out, the volume of the drop on the SL surface increases.

Picture changes in the case of macroinhomogenity appearing, which is the oxidizer particle. In that case the nonequilibrium state appears, and the particle is transferring to the new equilibrium state – the II equilibrium state. At this state breaking away of the particle becomes possible. Transferring of the particles state is accompanied with change of metal burning mode – from the heterogeneous to the gas-phase [15]. Connection of the agglomerating particle with the SL elements due to capillary forces ensures residence of the particle in this state for some time. The value of this time significantly less than the time needed for burn out of the "pocket". If the degree of nonequilibrium state of the particle is rather high that separation forces are capable of performing a work on its separating from SL elements, breaking away of the particle is implemented. This corresponds to the "pocket" mechanism of agglomeration.

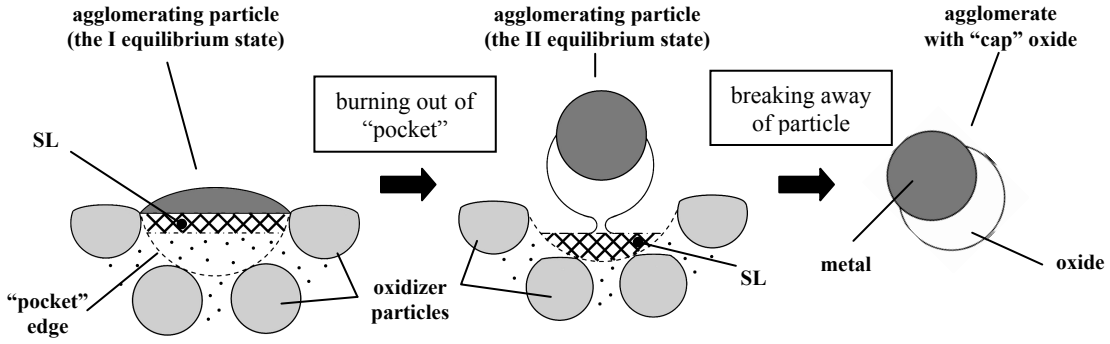

Figure 2: Scheme of the "pocket" agglomeration mechanism

If after burning out of "pocket" the particle does not leave the surface, it is moving along the "interpocket bridge" to the next "pocket" where it is merging with agglomerating particles of new "pocket" ("interpocket" merge). This process can occur many times, herewith size of the particle increases significantly (Figure 3). Unlike the "pocket" agglomeration mechanism the residence time of particle staying in the II equilibrium state is comparable with the time needed for burn out of "pockets". Moreover, agglomerates forming on the "interpocket" mechanism can have "matrix" structure [8].

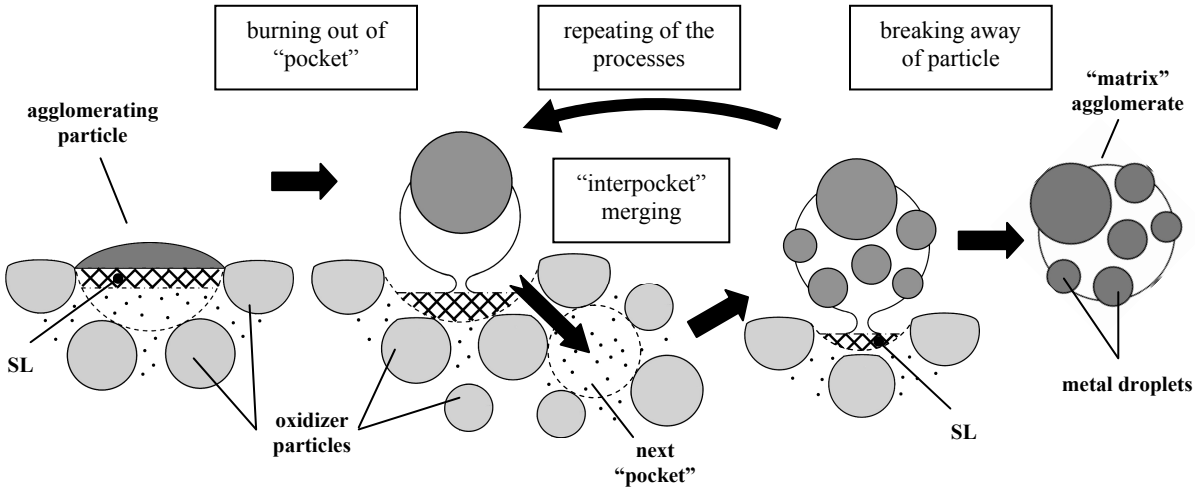

Figure 3: Scheme of the "interpocket" agglomeration mechanism

It was established experimentally that realization of "pocket" or "interpocket" agglomeration mechanism depends on chamber pressure. In the low-pressure area agglomerates are forming by both the "pocket" and "interpocket" mechanisms while in the high-pressure area agglomerates are forming mainly by the "pocket" mechanism of agglomeration [8].

2.4 Evolution of agglomerating particles

It was established that agglomerating particles located on the outer SL surface undergoing a set of physical and chemical transformations leading to chemical composition, structure and temperature changes, i.e. particles participate in the *evolution process*. Most significant indications of the evolution process are: decrease over time of

the metal value, influence of tensile accelerations on chemical composition, oxide removal, formation of "hollow" agglomerates, particles coalescence [16].

It is possible to offer the following set of mutually connected phenomena making evolution process (which are shown schematically on Figure 4):

- *Gas-phase combustion of metal*. Combustion in that mode results in formation of SOP and reduction of metal content in agglomerating particles, and later – in agglomerates (decrease of parameters Z_m и Z_m^a).
- *Chemical interaction condensed of Al and Al_2O_3*. This phenomenon results in formation of gaseous products which form gas cavities inside agglomerating particles. Periodic collapses of these cavities leads to oxide removal and reduction of oxide value in agglomerates (reduction of parameter Z_m^{ox}).
- *Change of particles structure.* Changes in particles structure are connected with changes in fraction of metal and oxide drops, as well as gas bubble. Parameters of the structure are determined mainly by surface properties of particles components.
- *Feeding and merging of agglomerating particles*. Connection of agglomerating particle with the SL leads to enlargement of particles at the expense of taking up SL "substance" and merging of adjacent particles. Obviously the particles enlargement depends on duration of the evolution process.

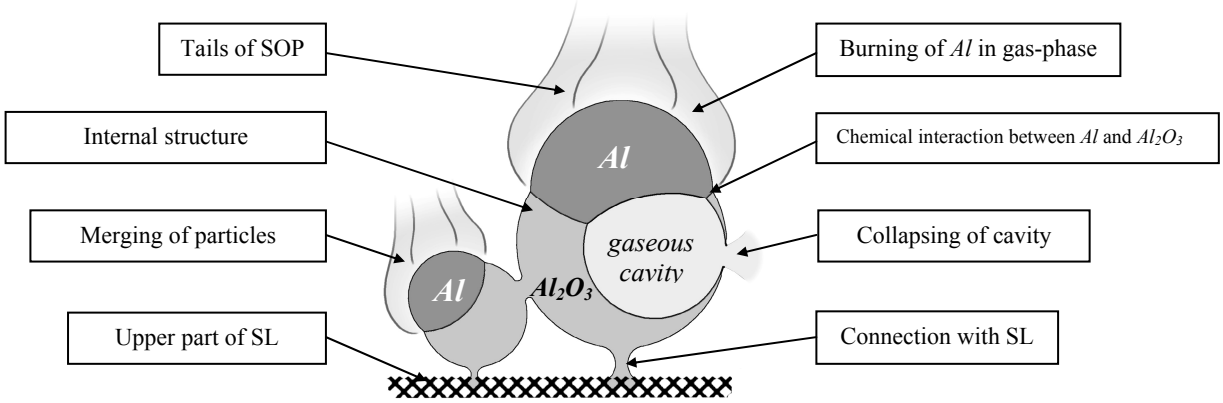

Figure 4: Scheme of evolution process of agglomerating particles on propellant surface

Duration of the evolution process of the agglomerating particle depends on its residence time on the SL surface in the II equilibrium state, which in turn depends on agglomeration mechanism. As mentioned above, for the "pocket" mechanism this time significantly less than the time needed for burn out of the "pocket", while for the "interpocket" mechanism it is comparable with the time needed for burn out of "pockets".

2.5 Breaking away of agglomerating particles

Possibility of the breaking away of agglomerating particles is connected with capability of separation forces to perform a work on separating the particle from the SL elements. In other words, the breaking away of the particle is connected with its impossibility to maintain the equilibrium state in specific conditions (at action of aerodynamic and mass forces). It is considered that following causes lead to the breaking away of agglomerating particles [15]:

Dynamism of the burning process. The breaking away takes place in the case, if velocity of oxidizer particle emergency is high enough, and external forces are able to perform work on separating the particle from the SL. This situation takes place at the "pocket" mechanism implementation.

Insufficient contact area. In the case of large particles, reduction of contact area leads to impossibility maintaining the equilibrium state of particle. This situation is typical for the "interpocket" mechanism.

3. Modeling of the agglomeration process

According to accepted methods, model of the agglomeration process is the result of synthesis of following separate models:

- The model of composite solid propellant structure [17],
- The model of formation of size agglomerates [15],
- The model of agglomerating particle evolution [16].

The model of composite solid propellant structure ensures determination of the size distribution functions of "pockets" and of oxidizer particles forming each "pocket" size. Moreover the model allows determining fraction of the "pockets" in propellant. Thus, it is possible to determine the fraction of initial metal in propellant used to form agglomerates (parameter Z_m^a).

The model of formation of size agglomerates allows determining the size distribution function of agglomerates. The model includes modeling of particles breaking away from SL, which in turn ensures determination of agglomeration mechanism depending on propellant composition and chamber pressure.

The model of agglomerating particle evolution provides predicting changes in properties of particle during its residence on the SL. The model includes mathematical descriptions of gas-phase burning of metal, chemical interaction between Al and Al_2O_3, structure of agglomerating particle, feeding by liquid substances from SL.

At this stage the ratio between metal and oxide in the SL was determined at usage of experimental data for combustion of various propellants in acceleration field. If tensile accelerations exceed some limiting value, then duration of evolution is negligible, and chemical composition of agglomerates corresponds to the ratio between metal and oxide in the SL. It is shown that at accelerations absence up to 25% by mass of metal in agglomerating particles burns in gas-phase mode during evolution [18]. Thus it was assumed that at zero accelerations evolution duration at realization of the "pocket" mechanism is determined by the time needed for burn out of 25% by mass of metal.

The model of agglomerates formation is described below:

1. Based on the data of propellant composition, modeling of solid propellant structure is performed, and the size distribution function of "pockets" is found.
2. Based on the data of propellant burning rate and external conditions, modeling size distribution function of agglomerates is performed. Moreover logging the data of quantity and sizes of "pockets" participating in each agglomerate formation is carried out.
3. For the agglomerate having any size D_i, new size distribution function of "pockets" participating in its formation is found based on the log of the quantity and sizes of "pockets" participating in each particle formation (see above). The new function contains in implicit form the conditions of breaking away of considered particle.
4. Based on previously obtained data, modeling of agglomerating particle evolution is carried out. Herewith the size of "pocket" is selected randomly based on the size distribution function obtained on step 3. If agglomerate is formed only from one "pocket", the "pocket" mechanism of agglomeration is implemented, and evolution duration is determined on the base of experimental data [18]. If agglomerate is formed from few "pockets", the "interpocket" mechanism is implemented, and the evolution modeling is performed until the agglomerating particle has not reached the D_i in size.
5. At varying of D_i and repeating of steps 3 – 4, this scheme can be expanded to the full range of agglomerate sizes.

4. Results of the model analysis

The results of the numerical analysis of formation of size agglomerates model correspond to the experimentally fixed features: agglomerates are formed mainly by the "pocket" mechanism in the high-pressure area and by both the "pocket" and "interpocket" mechanisms in the low-pressure area. As a consequence, there is the unimodal character of the density distribution function of agglomerate sizes in the high-pressure region (Figure 5-a) and the bimodal character of this function in the low-pressure region (Figure 5-b).

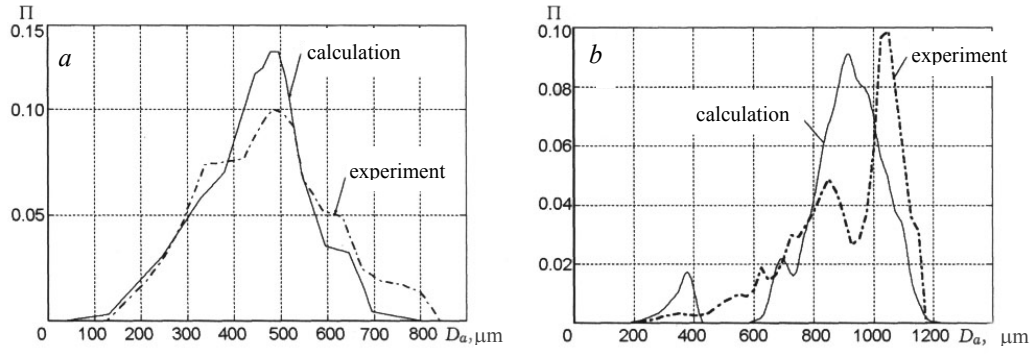

Figure 5: Smoothed density distribution functions of agglomerate sizes at pressures P = 6.2 MPa (a) and P = 0.4 MPa (b) [15]

Determination of the agglomerates chemical composition (Figure 6-a) results in the following:

– The discrepancy between the calculated and experimentally obtained data can be explained by the following: at low pressures changes in the propellant burning rate lead to changes in the SL structure (size and amount of pores), which in turn influence on parameters of the heterogeneous mode of metal burning. Thus for adequate modeling of agglomerates chemical composition in low-pressure area, it is necessary to develop of mathematical model of the heterogeneous combustion of metal inside the SL.

– In the high-pressure area the agglomerates chemical composition almost does not depend on the chamber pressure. It is connected with constancy of the SL chemical composition and significantly shorter duration of the evolution process at the "pocket" mechanism domination. Composition of SL does not depend also on pressure.

The model of the evolution of agglomerating particles allows also determining the temperature of particles (Figure 6-b). According to this model the particles temperature corresponds to the temperature of equilibrium evaporation of metal at gas-phase burning.

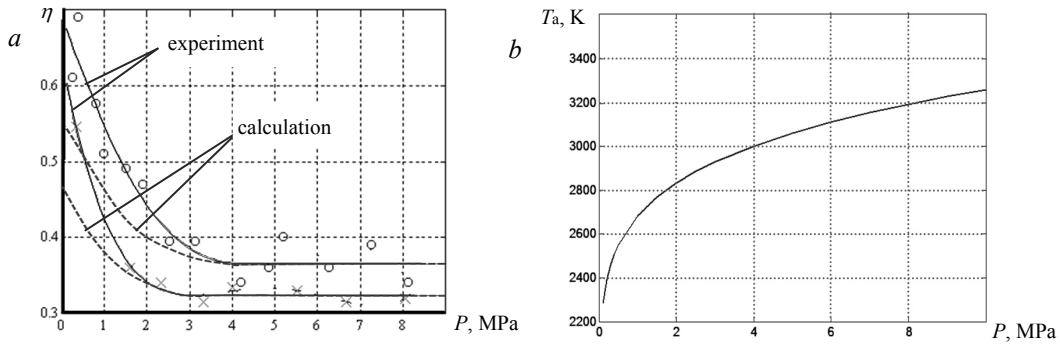

Figure 6: Dependencies of the mass fraction of oxide in agglomerates η (*a*) and agglomerate temperature T_a (*b*) on chamber pressure *P*

The results of the modeling of the agglomerates structure and their comparison with experimental data allowed to make the conclusion of adequacy of mathematical model (Figure 7). The model allows describing the structure of all the agglomerates types including "matrix" and "hollow" agglomerates.

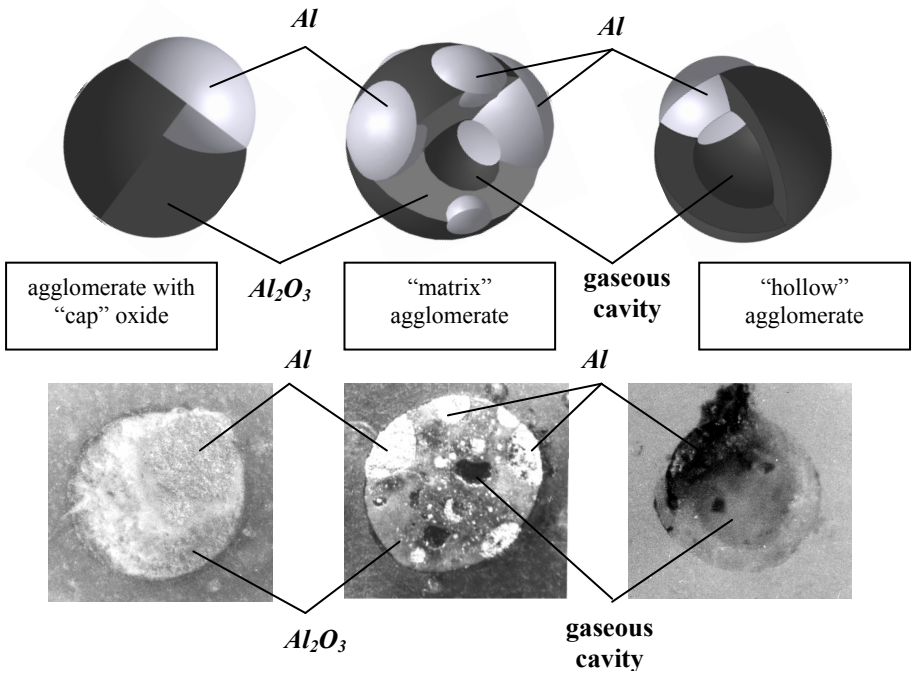

Figure 7: Results of modeling of agglomerate structure and comparison with experimental data

Conclusion

The basic results of the present work could be defined as follows:

- The physical picture of the agglomerating process is developed for propellants based on AP, ADN, HMX, inactive binder, and nanoaluminum.
- The analysis and synthesis of mathematical models is carried out, that provides prediction of the agglomeration process parameters.

- The conclusion on the need for a model of metal combustion in heterogeneous mode inside SL is made.

Obtained results indicate the rightfulness of the accepted physical picture, and it is shown that solution of the agglomeration modeling problem is fundamentally possible for other types of metalized solid propellants.

Further work will be directed on development of the mathematical model of metal combustion in heterogeneous mode inside SL. It is assumed that such model will allow predicting the chemical composition of agglomerate with higher accuracy as well as describe the effect of the agglomeration process on the propellant burning law.

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