Condensed Combustion Products at the Burning Surface of Aluminized Solid Propellant

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Experimental results are presented on the formation of condensed combustion products (CCPs) at the burning surface of aluminized solid propellants. A number of experimental techniques were developed for describing the characteristics of the CCPs as a function of the oxidizer particle size and pressure. The results of this investigation provide qualitative descriptions of the CCPs formed at the propellant burning surface as functions of oxidizer particle size and pressure.

Nomenclature

a_k	= oxidizing potential of gas mixture (mole share of oxidizing components in the mixture)
D	= diameter of agglomerate
D_{43}	= mass-medium diameter of agglomerates
D_{43}^{AP}	= mass-medium diameter of ammonium perchlorate particles
d	= diameter of fine oxide particle
d_{43}^{HDO}	= mass-medium diameter of fine oxide particles
$F_m(D)$	= mass function of agglomerate size distribution
$f_m(D)$	= mass function of agglomerate size distribution density
$f_m(d)$	= mass function of fine oxide particle size distribution density
P	= pressure
r	= propellant burn rate
T	= temperature
Z_m	= share of unburned metal in the agglomerates relative to the initial aluminum in the propellant
Z_m^a	= share of initial metal in the propellant used to form the agglomerates as a whole
Z_m^{HDO}	= share of initial metal in the propellant used to form the fine oxide particles
Z_m^{ox}	= share of initial metal in the propellant used to form oxide in the agglomerates
γ	= edge angle of wetting
η	= mass share of oxide in agglomerates

Introduction

THE presence of metal fuel (MF) in solid rocket propellants (SRPs) greatly complicates the propellant burning process. The metal's most important combustion feature is the formation of condensed combustion products (CCPs). The properties of these products influence a number of phenomena that determine the quality of the propellant–motor system: propellant burning rate, losses in specific impulse, slag deposition in the motor chamber, effects of combustion products on the inert motor components, and stability of motor operation. The CCP properties are acquired during completion of the MF combustion process, i.e., the physical and chemical transformations of the metal particles (while they are) in the motor chamber.

The overall combustion process can be divided into two stages, depending on where the process occurs: in the condensed phase of the burning propellant or in the two-phase flow in the combustion chamber. The first stage includes the formation of CCPs near the burning propellant surface. The second stage consists of the evolution of CCPs in the two-phase flow during the motion of the products. This paper is devoted to studying the first stage of the combustion process. A brief description of the results obtained by many researchers in studying this process is presented in this section.

In the first stage of the combustion process, the key phenomenon is the agglomeration or coagulation of the condensed products in the surface layer of the burning propellant, which then supplies these products to the gas phase. The agglomeration phenomenon was described first in the works[1] of the Institute of Chemical Physics of the USSR Academy of Sciences in the early 1960s. In the following years, practical applications of solid propellants required wider investigations of these processes. These studies included the acquisition of experimental data, the analysis of these data, and the development of techniques for predicting agglomerate characteristics, such as parameters determining the chemical composition and structure of agglomerates, agglomerate size distribution, and relative quantity of agglomerates in the two-phase flow of combustion products.

The purpose of these experimental studies was to obtain information on both micro- and macroregularities of the agglomerates. The microregularities are defined as those properties that determine the nature of agglomerate formation. On the other hand, macroregularities are those properties that relate the agglomerate characteristics to the propellant composition parameters and the combustion conditions. A set of techniques has been developed to solve these problems.[2−6]

Structure of Agglomerates

There are two basic concepts for the agglomerate structure. In the first concept, it is assumed that agglomerates contain other ingredients (the binder or its degradation products and the oxidizer) in addition to the metal and its oxide and that they may be nonspherical.[7] According to the second concept, the agglomerates only consist of metal and oxide drops.[6,8−12] The different concepts, both of which are observed experimentally, apparently are caused by changes in propellant formulations, the conditions of burning, and, in a number of cases, the inherent characteristics of investigation techniques. Both a decrease in operating pressure and inclusion of metal in homogeneous propellants contribute to the generation of the first type of agglomerate.[7] It also has been found that the second type of agglomerate is more prevalent with most propellants and for a wide range of burning conditions. Some experiments[6,11] have shown that the structure of the agglomerates may differ and these differences depend on the propellant properties and the burning pressure.

Conditions of Agglomerate Formation

At present, it generally is assumed that the metal particles are retained, move, and fuse on the burning propellant surface.[7,13-16] It is assumed that a necessary temperature condition for fusing is when metal particles reach their melting point. The fact that the oxide film has a higher melting temperature is not an obstacle to fusing because the film may be cracked.[5] The temperature at surface of the burning propellant is a primary factor in the agglomeration process. If this temperature is lower than the metal melting temperature, then particle fusion is impossible. In this case, the products have an irregular shape and incorporate both the binder materials resulting from incomplete gasification and the metal particles. This situation occurs, for example, in burning of double-base solid propellants.[7] In the case of binders that are difficult to gasify, the metal burns principally in regions where the binder and the oxidizer are in contact. Hence, it seems possible that the simultaneous release of binder and initial metal fragments into the gas phase could lead to the formation of the first type of agglomerate. In the gas phase, the pyrolysis of binder is completed and the possibility arises for the particles to ignite and interact with each other to complete the metal combustion process.

In Refs. 17 and 18, in which the framework for the pocket-type mechanism of agglomeration is justified, it is assumed that initially all of the metal particles in the propellant contact each other. During propagation of the combustion wave, bridges between the particles develop and obstruct the release of particles into the gas phase. As soon as ammonium perchlorate (AP) particles appear (the pocket is completed), the bonds between agglomerating particles and the condensed phase of the burning propellant are broken, producing a particle. As a result of the fusion of all of the particles, the pocket is fed into the gas phase. It is noted in Ref. 13 that, in case of binder melting, an additional effect of capillary forces is involved and contributes to retention of the particles in the surface layer of the burning propellant and to setting up contacts between particles.

The results obtained in a number of works, for instance, Refs. 6 and 9, support the concept that the agglomerating particles also are burning. This concept leads one to look differently at the conditions under which the agglomeration process occurs. In fact, the oxide melts when the particles are ignited. Thus, the ambient temperature is not the only criterion for particle fusion. The surface layer could possess a number of specific properties that ensure that the high-temperature particles are retained. In a number of works,[10,11,19] a suggestion has been made that specific structures are being formed in the surface layer. Burning of agglomerating particles then could change the properties of the agglomerates.

Effect of Propellant Composition and Burning Conditions on Size and Quantity of Agglomerates

Agglomeration is one of the manifestations of the solid-propellant burning process and it is quite natural that the characteristics of the agglomeration process depend on the propellant composition and burning conditions. When considering the effect of the propellant composition, one should distinguish the following: 1) particle size and concentration of the dispersed oxidizer (DO) and MF and 2) the types of DO, fuel, and binder. The particle size distribution is a another parameter characterizing dispersed systems; higher dispersions correspond to smaller particle sizes being present in the propellant. Currently, it generally is accepted that the oxidizer particle size distribution exerts the most important influence on the characteristics of the agglomeration process.[7] A decrease in the DO dispersion leads to an increase in the agglomerate size. In the works of Grigoryev et al.[17] and Cohen[20] devoted to a systematic investigation of the effect of the propellant structure on the agglomeration process, the authors conclude that oxidizer particle size is the decisive characteristic. In Refs. 6 and 12, the DO dispersion is shown to produce an effect on the quantity of agglomerates as well, decreasing the quantity simultaneous with a decrease in oxidizer particle size. It also is assumed that increased initial MF dispersion and concentration accelerate the agglomeration process.[7,14]

Data relating the influence of oxidizer content on the agglomerates are not available. It can be supposed that the effect of that factor is of a contradictory nature because it influences both the propellant burning rate and its structure. It should be stressed that a change in the propellant ingredients inevitably causes changes in the propellant energy-producing capacity.

Different substances may be employed as oxidizers. As a rule, they are perchlorates, nitrates, and nitramines. At present, AP, ammonium nitrate, ammonium dinitramide (ADN), and cyclotetramethylenetetranitramine (HMX) are the most widely used oxidizers. According to published results, it can be assumed that the effect of the oxidizer on the agglomeration process results from the following: effect on the propellant burning rate, the possibility of a molten layer forming on the burning propellant surface, and a change in the properties of the surface layer of the burning propellant.

As a rule, it is thought that an increase in the propellant burning rate leads to a decrease in agglomeration intensity.[7] The universal applicability of this assumption is questioned by the results in Ref. 13. The data obtained in Refs. 13 and 21 show that the formation of oxidizing substances in the melted state increases mass-medium diameter of agglomerates by 2–3 times. In Refs. 6, 11 and 12, the change in surface-layer properties is shown to change the agglomeration mechanism. It is obvious that a change of the fuel type should influence the characteristics of the agglomeration process. (In Refs. 13 and 21, it is shown that substituting magnesium for aluminum decreases the agglomerate size.) However, note that both current propellants and future propellants will use only aluminum as an MF. The effect of the binder properties on the agglomeration is related, as a rule, to the ratio of carbon to easily gasifiable elements in the binder.[7] For propellants with moderate MF content (up to 25%), an increase in carbon content is considered to be a factor contributing to agglomerate size growth.[13,21] For the propellants with a high MF content, the inverse effect is supposed to occur.[13,21]

As for the effects of combustion conditions, the primary factors are the pressure in the combustion chamber, the character of the two-phase flow, and the magnitude and direction of the motor acceleration. Most of the works published to date indicate that a pressure increase is accompanied by a decrease in the agglomerate size.[7] This effect is explained by the dependence of the propellant burning rate on the pressure and the fact that an increase in burning rate decreases the degree of agglomeration. At the same time, it was found that the agglomerate particle size does not depend on pressure for a rather wide range of propellant compositions.[17] For propellants with high metal content (more than 25% by mass), the complex character of such a dependence has been determined.[13,21] Both an increase and a decrease in the agglomerate dispersity may accompany a pressure increase. Similar effects may take place in the combustion of propellants with lesser metal content as well.[6,10] Noting that the agglomeration process occurs in the surface layer of the burning propellant, one would assume that gas flow effects are determined primarily by the longitudinal component of the gas flow past the propellant surface. In Refs. 7 and 22, this effect of the longitudinal component has been confirmed experimentally. The dependence of the agglomerate size on the gas flow velocity has a complex character.[7] Initially, the sizes grow with increased velocity, but then decrease. Thus, it is necessary to underscore the following: Such an effect is possible when the longitudinal component of the gas flow velocity is more than, or at least of the order of, the perpendicular velocity component at distances from the burning propellant surface that are comparable to the size of the growing particles. The dimensions of the motor have a large influence on this condition. As a rule, for large rocket motors, this condition cannot be realized.

The number of experimental studies devoted to investigating the effects of the magnitude and direction of the motor acceleration on agglomeration is small. A number of studies[23-27] have investigated burning-rate evolution under the influence of acceleration, where the effects of acceleration are related, to some extent, to the behavior of the condensed products, both in the surface layer and close to the burning-propellant surface. It generally is accepted that the increase in the force perpendicular to the surface contributes to retention of the condensed products on the burning-propellant surface and, in the limit, leads to a liquid layer forming on the surface.

Formation of Highly Dispersed Oxide (HDO)

At present, it is commonly agreed that the condensed products consist of both agglomerates and very fine particles, even close to the burning-propellant surface. Even if the size of agglomerates reaches hundreds or even thousands of micrometers, the HDO particles have sizes of the order of 1μm. No work in which the HDO dispersion has been investigated under the conditions mentioned is known to these authors. It may be supposed that the primary source of the HDO close to the burning propellant surface is the metal that is not involved in the agglomeration process.

Several papers contain data on HDO properties in the final products of propellant combustion.[28−30] These papers point out that the HDO particle size depends both on propellant properties and on the pressure in the chamber; the mass-medium diameter of particles being in the range of 2–5 μm. However, because HDO is formed during burning of both the nonagglomerating metal and the metal incorporated in the agglomerates, these observations cannot be used readily to characterize the fine oxides in the region close to the burning-propellant surface.

Purpose of This Investigation

This literature analysis strongly indicates that further the study of the condensed-product formation process should focus primarily on obtaining high-quality experimental data close to the burning-propellant surface. This lack of sufficient data is the primary factor restraining the improved understanding of the principal processes in the combustion of metals as a propellant ingredient. To obtain reliable data, the investigation should meet the following requirements: completeness of parameters to be studied, systematic study of parametric variation, and a sufficient amount of experimental data for providing reliable results.

It is well known that changing the oxidizer particle-size distribution is one of the most powerful tools for influencing the agglomeration process. Therefore, within the framework of the present investigation, the characteristics of the products close to the burning-propellant surface were determined as a function of the oxidizer particle size at various pressure levels. It was anticipated that the chemical composition of the propellant investigated would stay the same, and that the investigation would consider both the agglomerates and the fine oxides.

Characteristics of Propellants

Propellant compositions based on isoprene rubber as a fuel binder and AP as an oxidizer were chosen for this investigation. The different propellants have the same percentages of components and differ only in the oxidizer particle-size distribution. The mass content of the various propellant components is given in Table 1. The spherical aluminum used in these compositions had a maximum particle size of 50 μm and the following distribution of particle sizes: 0–10 μm (67% by mass), 10–20 μm (16%), 20–30 μm (9%), and 30–50 μm (8%). Four fractions of varying AP particle sizes were used: Fraction 1 had particles of about 1-μm diam, fraction 2 had particles less than 50 μm, fraction 3 had particles from 160 to 315 μm, and fraction 4 had particles from 400 to 600 μm. These four AP fractions were mixed into five propellant formulations in varying proportions, as shown in Table 2.

Results of the thermodynamic analysis for combustion products of the propellants are presented in Fig. 1, which shows the dependence of the oxidizing potential and the temperature of gaseous combustion products as a function of the share of the aluminum burned $(1 - Z_m)$.

Investigation of Agglomerates

The theory of agglomeration should be developed on the basis of reliable experimental data, which must be highly representative and informative. This requirement places special constraints on the experimental technique employed to obtain information on the physicochemical characteristics of the agglomerates. To ensure the optimum combination of representative conditions, valid information, and simplicity of testing, a particle quench-collection technique

Table 1 Propellant composition

Component	Content by mass, %
Al	24
AP, NH_4ClO_4	64
Isoprene rubber —CH_2—C = CH—CH_2— $\vert$ C	2.6
Additives	0.3
Surface active material	0.1
Oil, $C_{19}H_{35}$	9

Table 2 Parameters of propellant oxidizer

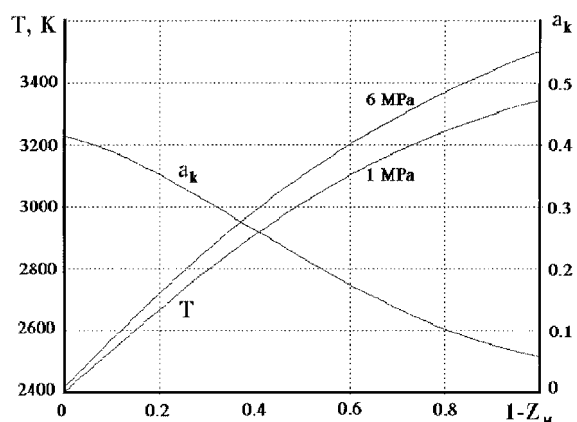| Propellant	AP fraction (proportion, %)
N1	Fr. 1–Fr. 2 (50–50)
N2	Fr. 2 (100)
N3	Fr. 2–Fr. 3 (40–60)
N4	Fr. 3 (100)
N5	Fr. 4 (100)

Fig. 1   Results of thermodynamic analysis.

was employed in combination with a constant-volume bomb (CVB) to burn propellant samples and collect particulate combustion products. Particles having sizes greater than 30 μm were considered to be agglomerates.

Investigation Technique

The CVB technique used in investigating the agglomerates is based on quenching and then collecting particulate products from the process of propellant sample burning. The general scheme of the experiments is shown in Fig. 2. Small samples of propellants are burned in the CVB filled with inert gas, either helium or nitrogen. The mass of the propellant samples does not exceed 2 g, which ensures that the pressure in the bomb is constant within 10% during combustion. The samples are parallelepipeds having dimensions of 5, 5, and 10–20 mm. The side surfaces of the propellant samples are coated, which ensures layer-by-layer burning of samples from only one end. The thickness of the coating is chosen to ensure that its destruction rate is close to the propellant burning. The burning of samples takes place on the side with the smallest surface area. Ignition of the samples is accomplished by heating a filament with an electric current. Pressure changes in CVB are recorded and the data are used to determine the propellant burning rate.

Quenching of agglomerates was accomplished using either an inert liquid (alcohol) or an inert gas in CVB (helium, nitrogen). In the first case, a vessel with an inert liquid was placed at the required distance from the burning-propellant surface. In the second case, the quenching and freezing of the agglomerates was done with inert gas in CVB; they are subsequently removed from the CVB with the help of a special container.
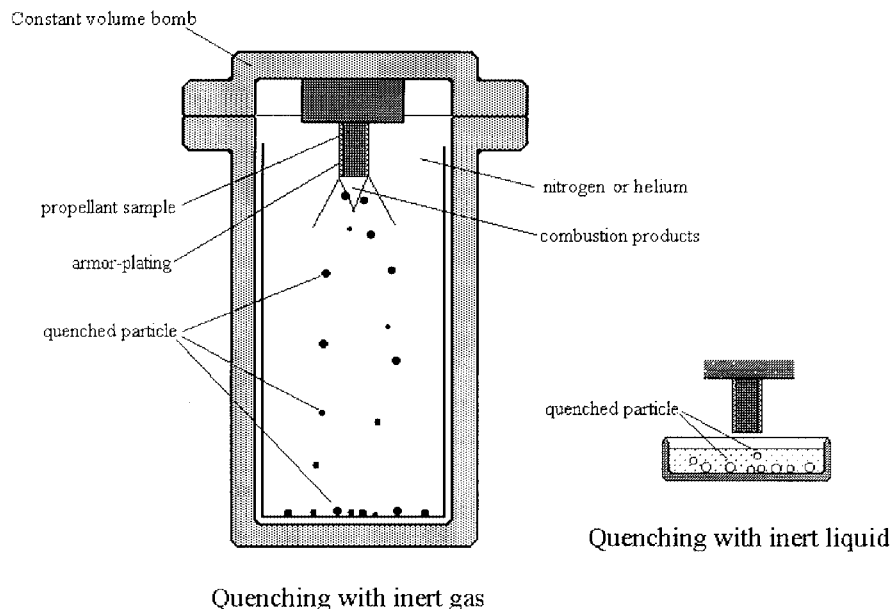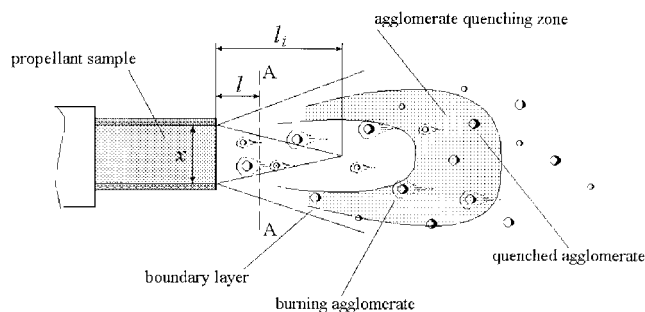
Fig. 2   Experimental method.

Fig. 3   Quenching of agglomerates.

In both these techniques, the agglomerate quenching occurs at some distance from the burning surface. This distance should be as short as possible to minimize potential changes in agglomerate properties, which occur after they separate from the propellant surface and before they are quenched. When using an inert liquid, the size of the quenching zone is defined readily by the distance between the propellant surface and the location of the liquid surface. When freezing with an inert gas, this separation effect is minimized by using a small burning surface area (5×5 mm) for the propellant sample. Here, the actual quenching zone has a complex spatial form, as shown in Fig. 3. The agglomerate quenching occurs within the mixing boundary layer formed between the flowing products of propellant combustion and the surrounding stationary inert gas. An analytical estimate for the length of the initial adiabatic portion of the flow, l_i, gives $l_i = 3.6x$ for helium and $l_i = 0.4x$ for nitrogen. Here, x is the minimum cross-sectional dimension of the propellant sample. The magnitude of l_i is a weak function of pressure. Precise determination of the location of the agglomerate quenching zone in inert-gas freezing does not appear to be possible. Therefore, sampling conditions for all of the particles taken as a whole should be averaged and the agglomerate sampling zone imagined as a flat surface A-A. The location of that sampling surface relative to the burning surface (distance l in Fig. 3) has been determined experimentally by comparing experimental results using both quenching methods. To estimate the value of l, the following relations have been obtained: When helium was used as an inert gas, $l = 1.2x$; when nitrogen was used, $l = 0.15x$.

The quench-collected agglomerates were subjected to particle-size and chemical analyses and their structural parameters were determined. The particle-size distributions were measured using a FRICH Analyzette 22 microanalyzer, which could measure particle sizes from 0.1 to 1160 μm. In reducing these data, a problem arises as to how to transfer the particle-size analysis data to high-temperature flow conditions. On one hand, one must account for the fact that the substance density increases with sample cooling; on the other hand, cracking occurs because of the effect of thermal strains in "freezing" the particles. As a result, their density decreases. On the whole, previous studies that compared the result of visualization and sampling found that particle sizes determined by the two techniques are approximately the same. This finding allows one to conclude that the data obtained in the particle-size analysis of the quench-collected agglomerates are consistent with the conditions in the high-temperature flow of the propellant combustion products. The (internal) agglomerate structure was investigated by studying the agglomerate microsections.[11] As stated earlier,[11] the structure of the quench-collected agglomerates corresponds to that which they have in the high-temperature flow of the combustion products.

The chemical analysis of quench-collected agglomerates was aimed at determining their aluminum and aluminum oxide content. The agglomerates were etched in diluted hydrochloric acid, followed by weighing the remaining oxide. This procedure must account for additional oxidation, which occurs during particle freezing and during contact of the particles with air during storage. This additional oxidation distorts the actual characteristics of the condensed products considerably. This phenomenon occurs because the agglomerates undergo extensive cracking produced from the high thermal strain effect. On the surfaces of a great number of cracks formed, the metal oxidizes, and the oxidation produces readily soluble amorphous aluminum oxide. This oxidation process takes place either when the particles contact the air or in the process of freezing during their contact with alcohol. This formation of amorphous oxide considerably distorts the real agglomerate parameters and should be considered when using quench-collection techniques. This additional oxidation affects about 26% of the metal in the agglomerates and is about the same for both particle freezing methods. For practical purposes, this additional oxidation is independent of the agglomerate particle-size distribution. Storing the samples for a few days does not noticeably increase the oxide content in the agglomerates. Long-term storage (a few months), however, results in substantial additional agglomerate oxidation and the agglomerates disintegrate.

As a result of the chemical and particle-size analyses the following primary quantitative characteristics of the agglomerates are defined: Z_m, Z_m^{ox}, Z_m^a, Z_m^{HDO}, η, and D_{mn} [mean diameters

of agglomerate samples determined by empirical functions of agglomerate mass distribution density according to their sizes $f_m(D)$].

$$D_{mn} = \left\{ \frac{\int_{D_{min}}^{D_{max}} D^{(m-3)} f_m(D) \, dD}{\int_{D_{min}}^{D_{max}} D^{(n-3)} f_m(D) \, dD} \right\}^{1/m-n} \quad (1)$$

where D_{min} and D_{max} are minimum and maximum diameters of agglomerates.

The parameters Z_m^a, Z_m^{ox}, Z_m, Z_m^{HDO}, and η have the following relationships:

$$Z_m^{ox} = 0.53 \, Z_m \eta / (1 - \eta) \quad (2)$$

$$Z_m^a = Z_m + Z_m^{ox} \quad (3)$$

$$Z_m^{HDO} = 1 - Z_m^a \quad (4)$$

Investigation Results

The analysis of the agglomerate structure established that the agglomerate is an aggregate of aluminum and its oxide drops. The oxide forms a cap, partially covering the metal drop. Gas cavities (or bubbles) sometimes are found on the interface of the substances in the agglomerates. The presence of these bubbles is evidence of chemical reactions between aluminum and its oxide flowing in the agglomerate and producing gaseous reaction products.[12,31] The agglomerate shape is characterized by a combination of spherical elements, which leads to the conclusion that the surface energy of the given system (agglomerate) is a minimum. This minimum energy, in turn, suggests viewing the agglomerates as an equilibrium dispersed system and that the agglomerate structure is controlled completely by the surface tension of the substances from which it is formed: aluminum and its oxide, both in the liquid state.

Analysis of the agglomerate microsections allowed the edge angles of wetting γ_1 and γ_2 (Fig. 4) to be measured as functions of the pressure as follows: $\gamma_1 = 26$ deg and $\gamma_2 = 41$ deg at the pressure of

6 MPa, and $\gamma_1 = 28$ deg and $\gamma_2 = 43$ deg at the pressure of 1 MPa. In measuring γ_1 and γ_2, the random agglomerate cross sections have been considered.

The mass functions of size distribution $F_m(D)$, and mass functions of size distribution density $f_m(D)$ for the agglomerates are given in Figs. 5–9. Note that the distribution density functions can be both unimodal and polymodal. The primary quantitative experimental data are presented in Table 3 (for 6 MPa) and Table 4 (for 1 MPa). A rather high degree of confidence in these data has been assured by making 10 determinations for each characteristic cited.

As an example, Figs. 10 and 11 show the dependence of the main agglomeration parameters Z_m^a and D_{43} on the mass-medium diameter of the dispersed oxidizer at 1 MPa. These data show the following nature of the dependence of the agglomerate parameters on the oxidizer (AP) particle size and pressure:

1) At a pressure of 6 MPa, the increase in the specific surface of the oxidizer in the propellant (in transition from composition N5 to composition N1) causes a monotonous decrease of Z_m^a, Z_m, Z_m^{ox}, and D_{43} values. It is significant that the values of Z_m^a and Z_m decrease by more than 20-fold. At the same time, the propellant burning rate increases monotonously and the change in oxide content of the agglomerates is insignificant.

2) At a pressure of 1 MPa, the character of these parameters assumes a peculiar behavior. With an increase of the oxidizer specific surface in the propellant, the values of Z_m^a, Z_m, Z_m^{ox}, η, and D_{43} first decrease monotonously (following the transition from composition N5 to composition N2), but at a much slower rate than at 6 MPa, and then (in transition from composition N2 to composition N1) all of the above parameters increase substantially. The corresponding propellant burning rate increases monotonously with increasing oxidizer specific surface.

From these results, one can conclude that the character of the agglomeration process depends both on the particle size of the oxidizer in the propellant and on the pressure.

Investigation of Fine Oxide Particles

The study of the fine oxide particles also focused on obtaining qualitative experimental information. This focus required conducting the appropriate representative analyses, making reliable measurements of various parameters, and determining exactly the location of the zone being studied in the propellant burning area.

Experimental Technique for HDO Particles

A new experimental technique was developed for studying HDO particles. This technique provided the means for obtaining information about the particle size and chemical composition of the HDO particles, and for scanning electron microscopy (SEM) studies of the particles. The layout of the experimental setup is given
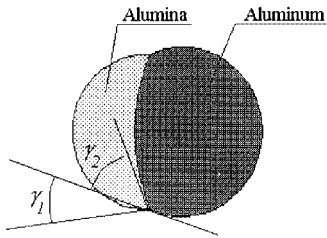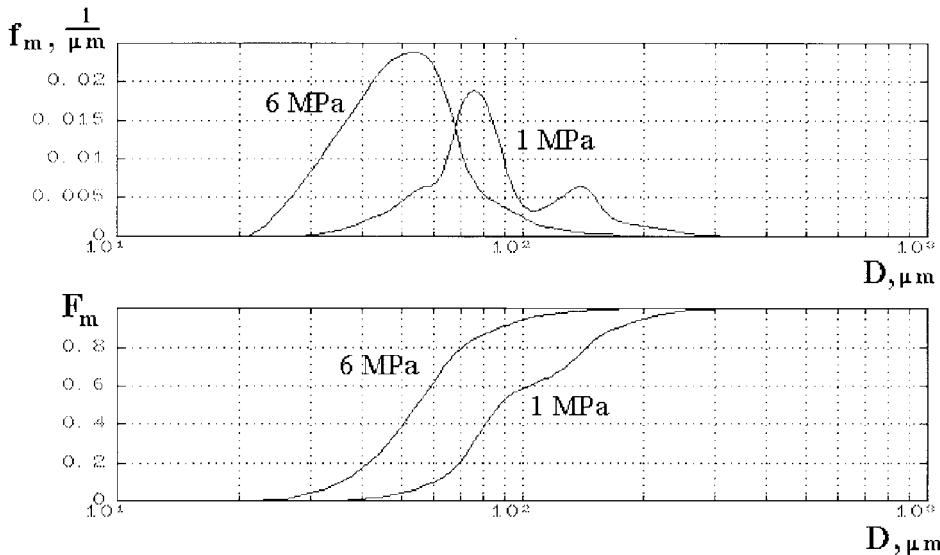
Fig. 4 Agglomerate structure.

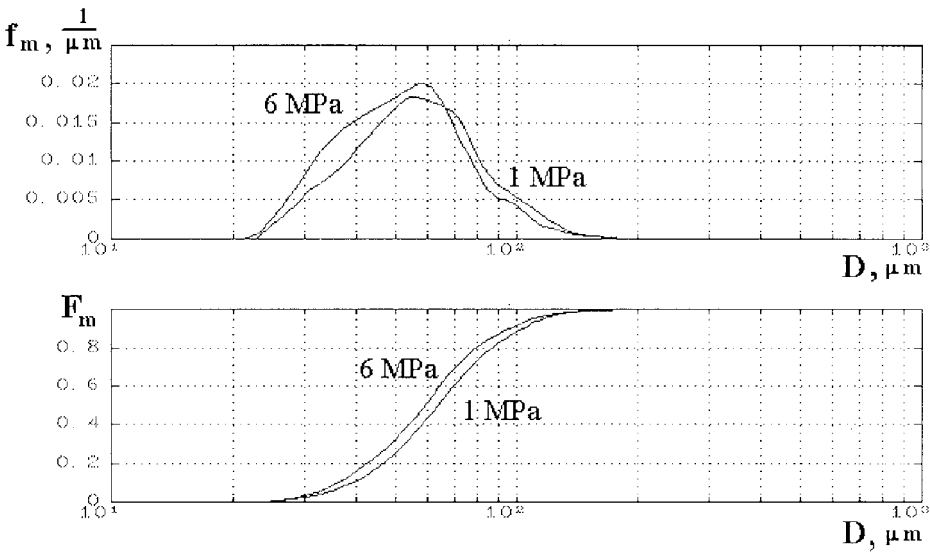Fig. 5 Agglomerate size distribution for propellant 1.

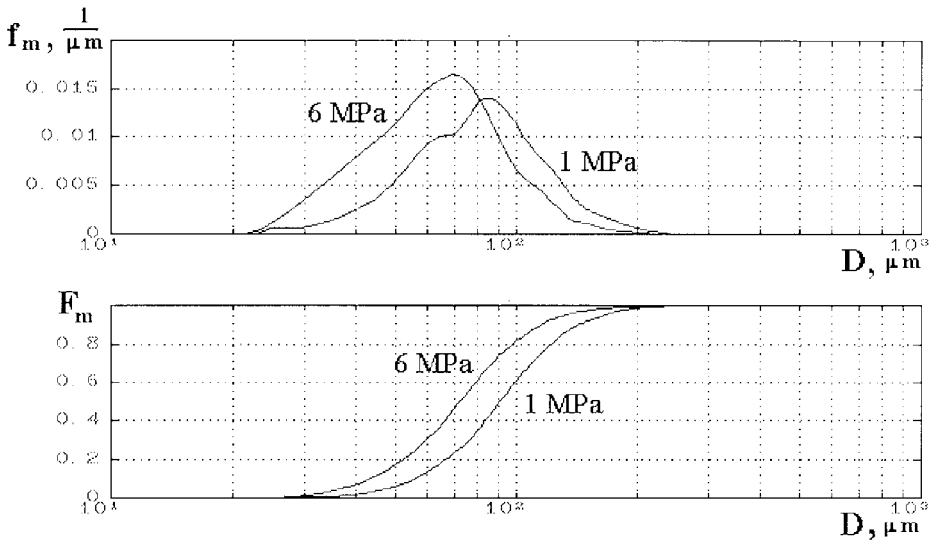**Fig. 6   Agglomerate size distribution for propellant 2.**

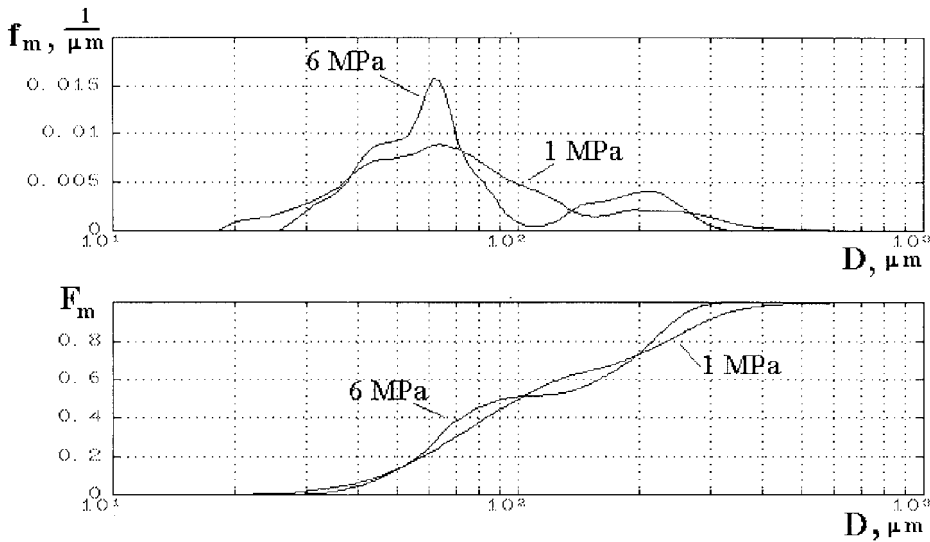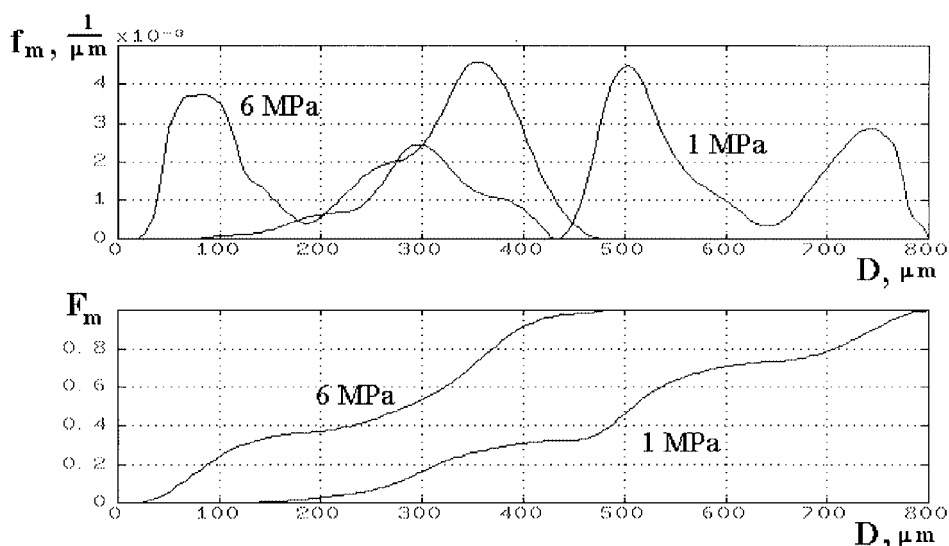**Fig. 7   Agglomerate size distribution for propellant 3.**

Fig. 8   Agglomerate size distribution for propellant 4.

Table 3 Experimental data for pressure 6 MPa

Composition	Z_m	Z_m^{ox}	Z_m^a	η	$D_{10}, \mu m$	$D_{32}, \mu m$	$D_{43}, \mu m$	r, mm/s
N1	0.011	0.002	0.013	0,256	37	51	59	58.4
N2	0.015	0.008	0.023	0,502	38	54	62	38.7
N3	0.036	0.011	0.047	0,366	45	66	77	28.2
N4	0.108	0.045	0.153	0,440	51	87	131	15.0
N5	0.254	0.090	0.344	0,401	53	143	250	8.1

Table 4 Experimental data for pressure 1 MPa

Composition	Z_m	Z_m^{ox}	Z_m^a	η	$D_{10}, \mu m$	$D_{32}, \mu m$	$D_{43}, \mu m$	r, mm/s
N1	0.29	0.045	0.335	0,227	67	90	107	34.0
N2	0.21	0.021	0.23	0,159	45	59	68	12.0
N3	0.32	0.045	0.350	0,210	59	84	98	6.1
N4	0.36	0.052	0.409	0,214	44	87	141	6.0
N5	0.39	0.063	0.452	0,234	263	430	504	5.9

Fig. 9 Agglomerate size distribution for propellant 5.
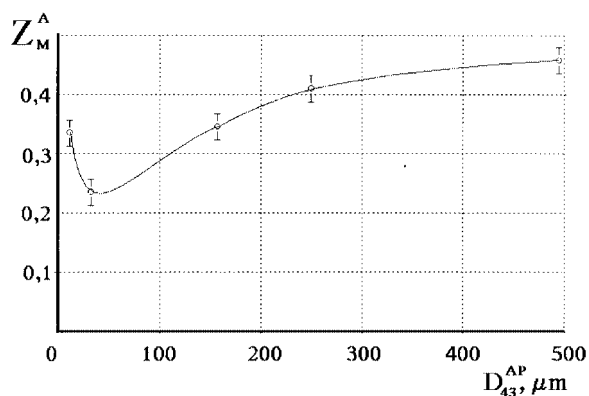
Fig. 10 Dependence of Z_m^a on D_{43}^{AP} at low pressure (1 MPa).
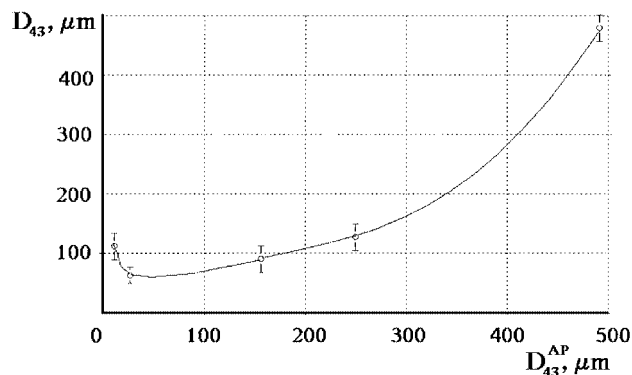
Fig. 11 Dependence of D_{43} on D_{43}^{AP} at low pressure (1 MPa).

in Fig. 12. In the CVB (2), a glass vessel (3) is inserted so as to fill the maximum possible inside volume of the CVB. It is necessary to avoid possible particle losses by their being removed from the vessel by flow from the pressure difference between the vessel and the CVB generated during propellant combustion. A layer of ice ∼5 mm thick (4) is frozen on the vessel walls to prevent particles from sticking directly to the vessel walls and to remove deposited particles from the CVB when the pressure drops. The propellant specimen (1) is placed inside the vessel and ignited with an incandescence filament. After combustion of the specimen and precipitation of the

condensed-phase particles onto the bottom and inner walls of the vessel, the gas-phase products are released from the CVB. Then, the particles can be extracted from the liquid by evaporation or filtering.

Because the CCPs contain both metal oxidation products and soot, it is possible that the presence of soot might distort the experimental data. Chemical analyses of the condensed products have shown that the carbon content in the sample is less than 0.5%. Thus, the presence of the soot in sampled particles can be neglected. The next issue considered was the time that the CVB must remain sealed after combustion is completed. It possible to estimate the particle precipitation time for spherical particles in gas after combustion is completed.
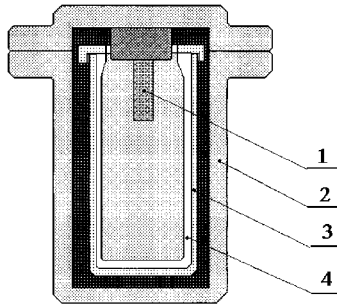
Fig. 12   Experimental setup.

Table 5   Experimental data

Propellant	Z_m^{HDO}	D_{43}, μm	d_{43}^{HDO}, mμm	r, mm/s	χ, %	f_{loss}^{HDO}, %
Baseline	0.36	370	820	5.7	95.3	13
N5	0.64	190	870	8.1	89.5	16
N2	0.97	50	530	38.7	71.0	30

Fig. 13   Histogram of HDO particle size distribution.

These estimates indicate that all particles larger than 0.5 μm will precipitate to the vessel bottom over the period of ~2 h.

A number of experiments have been conducted to confirm the efficiency of this technique. This technique has been tested using the working propellant compositions. It has been found that keeping the CVB sealed for 2 h after the specimen combustion is sufficient. Delays of more than 2 h do not increase the mass of the sampled particles significantly; i.e., as a rule, 93–98% of the total estimated mass and the parameters of the CCPs Z_m, Z_m^{ox}, and Z_m^a remain essentially constant after 2 h.

To investigate the HDO particles further, they were separated from the agglomerates by sifting through a sieve. The selected HDO particles actively stick together and form loose coagulants. The formation of these coagulants is determined by the condition of the particle surface, such as electric charge. To prevent this phenomenon when conducting dispersity analysis, the suspension of sampled HDO particles in water solution of special substances, e.g., sodium pyrophosphate, are exposed to ultrasonic dispersal. The ultrasonic power used was considerably less than that required for fragmentation of separated individual HDO particles. Note that the action of the ultrasound on the sampled HDO particles can causes reverse effect, that is, generating new coagulants. It was obtained experimentally that the latter effect takes place at rather long times of the procedure.

These phenomena are understood poorly and cannot be predicted precisely. The power of ultrasonic impact, ultrasonic frequency, and time of the procedure have been chosen empirically with the aim of obtaining HDO particle-size distribution functions as close as possible to the real ones with a minimum quantity of coagulants.

After dispersal, the initial mixture was extra diluted with water to obtain three samples of differing concentrations. Each sample was analyzed 10 times (10 parallel measurements were taken) in the Coulter-4 particle size analyzer for submicron particles, using a dynamic light-diffusion technique. The resolution range of this device is from 10 mμm to 10 μm. An example printout of the results obtained from this device is presented in Fig. 13.

Analysis of Experimental Data

The HDO particles have a regular spherical form with sizes of tens to thousands of nanometers (Fig. 14). To analyze the regularities of the HDO formation close to the burning propellant surface, particle masses and particle size distributions were compared as functions of pressure and DO properties for combustion of different propellants. Table 5 contains data from samples at 6 MPa for three compositions (N2, N5, and a baseline composition used for technique development). These propellant compositions essentially differ in the value of the parameter Z_m^a. Assuming there is a negligible loss of agglomerates, the share of unsampled (i.e., lost) HDO particles (f_{loss}^{HDO}) can be calculated in the following way:

$$f_{loss}^{HDO} = (1 - \chi)/Z_m^{HDO} \qquad (5)$$

where χ is a share of the CCP sampled in the experiment.

These experimental results (Table 5) show that a decrease in Z_m^a (i.e., an increase in Z_m^{HDO}) gives, as a rule, an increase in parameter f_{loss}^{HDO}.

Based on the measured histograms, the particle distribution functions f_m of the HDO particle distribution are plotted in Fig. 15
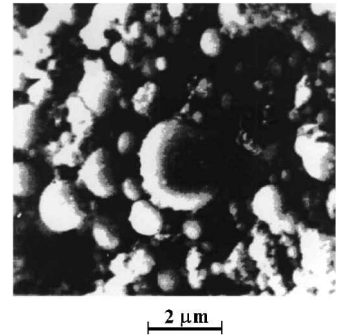

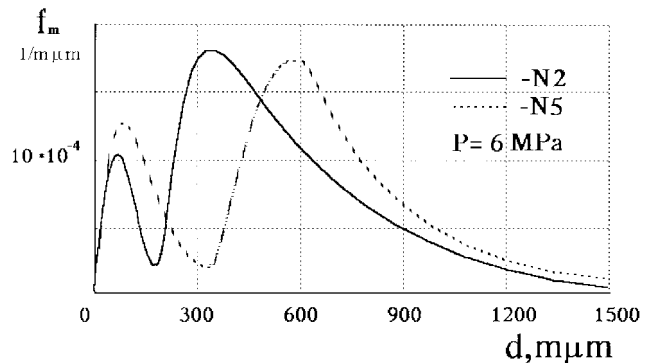Fig. 14   HDO particles.

Fig. 15   HDO particle size distribution.

for compositions N2 and N5 at 6 MPa. Apparently, these functions have a bimodal character. The first mode covers the size range of 20–200 mμm and the second covers 300–1000 m μm. The fraction of particles in the second mode dominates. Figure 16 shows the dependence of the HDO mass-medium diameter on the oxidizer mass-medium diameter at two pressure levels. With a decrease in the oxidizer particle sizes in going from composition N5 to composition N1, HDO particle sizes first increase, and then decrease. The pressure increase is also a factor contributing to a decrease in the fine-oxide particle sizes.

Physical Concepts of Condensed-Product Formation

These experimental results now make it possible to clarify the essential regularities of condensed-product formation close to the burning propellant surface.
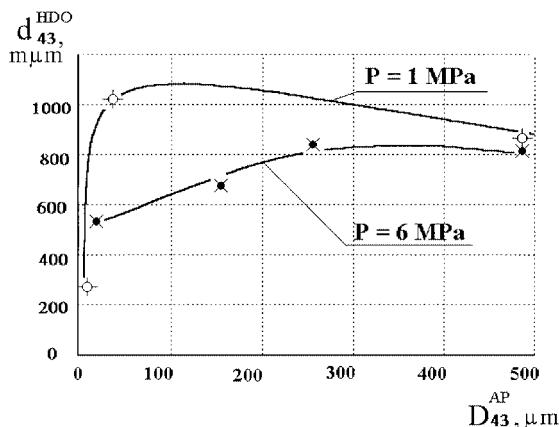
Fig. 16 Dependence of mass-medium diameter of HDO particles d_{43}^{HDO} on D_{43}^{AP}.

Fig. 17   Propellant structure.

Agglomerate Formation

A vital condition for the agglomeration process to occur is the formation of a specific structure, which has been named the skeleton layer (SL).[6,10,11,19] The SL is a gas-permeable three-dimensional structure that consists mainly of metal and its oxide, but also has a small amount of carbon elements, and forms on the upper portion of the burning propellant surface layer. A characteristic feature of the SL is the high adherence of its metal and oxide particle constituents. The lower SL surface can be considered as the zone where the degradation of the binder into gas-phase products and solid carbon elements basically is completed. On the upper SL surface (facing the gas phase), the smaller particles stick together to produce larger ones, which form the agglomerate flow when breaking away from the propellant burning surface. The SL provides for the two most important conditions of agglomeration: 1) contact between particles, and 2) retention of particles (including burning ones!) in the surface layer. One also may suppose that the MF participating in the SL formation participates in the agglomeration process as well. The physical principles of SL formation are discussed in Ref. 19. It was shown that the carbon skeleton (CS) is vital in SL formation. The evolution of the CS is determined by the properties of the polymer binder and the conditions under which it degrades.

In the burning of composite propellants, their structure exerts an essential influence on CS formation, and therefore on the SL. To describe their structure, it is appropriate to use such concepts as pocket and interpocket bridges (IPBs). The general idea for the pocket concept appeared in the work of Price et al.[32] in the mid-1960s. For mathematical modeling, the pocket concept was used first in the works of Cohen[20] and Grigoriev et al.[33] Introducing the pocket concept, in spite of its apparent conventional nature, has proved to be a fruitful idea in studying the agglomeration. As applied to actual propellant compositions, the following conditions are necessary for pocket formation: The oxidizer particles forming the given pocket must be comparable in size and the particular size of the pocket must be comparable to the oxidizer particle size bounding it and much larger than the initial size of the metal particle. The bridges represent the cells of the binder-fuel composition bounding separate pockets. They can be imagined as interlayers of propellant between oxidizer particles (Fig. 17). These interlayers burn in a medium rich in oxidizing gases, which hampers the formation of the CS. The pockets burn under different conditions, which make possible the formation of the SL. Thus, the proportion of pockets and the quantity of bridges should exert a considerable influence on the degree of MF involvement in the agglomeration process.

The extent of the growth of the agglomerating particles is determined by their residence time under on the SL surface. The analysis conducted to study the conditions under which particles break away from the SL surface shows that this time mainly depends on the character of SL heterogeneity and the dynamics of the burning process (burning rate).[34,35] It should be stressed that the metal particles participating in the agglomeration process also burn. Immediately after
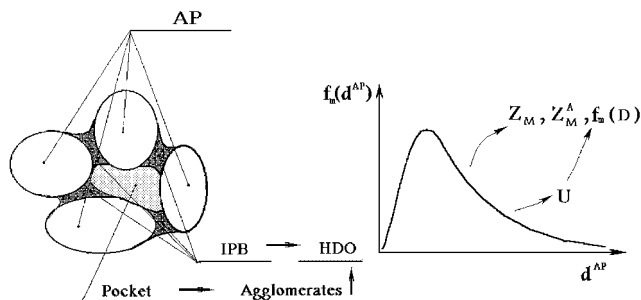
ignition, this burning proceeds in a heterogeneous mode. On reaching some temperature, the burning mode changes into a gas-phase mode.

Now consider how the agglomeration characteristics develop in the compositions investigated. The effect of propellant structure is seen distinctly at low pressure. Under conditions where the oxidizer particles provide for pocket formation, increasing the oxidizer specific surface increases the volume fraction of the bridges in the propellant mass. This causes a decrease in the parameters characterizing the MF fraction in the agglomerates (Z_m^a, Z_m, Z_m^{ox}) as shown in Table 4 by comparing composition N5 to composition N2. Examining these parameters for composition N1 shows that the finer oxidizer particles lose their ability to form pockets because of their small size, and the propellant undergoes a peculiar sort of homogenization. (In terms of the structural model, this homogeneous propellant consists of one infinitely large pocket). This behavior increases the fraction of MF participating in the agglomeration, as shown by comparing composition N1 with composition N2 in Table 4.

The relative oxide content in the agglomerates is determined mainly by metal burning in the heterogeneous mode. The results shown in Table 4 suggests that the metal fraction burning out in this mode increases following the increase in the pocket size. As the oxidizer specific surface increases, the propellant burning rate and the SL heterogeneity change. The combined effect of these factors is to decrease the agglomerate sizes as shown in Table 4 by composition N5 to composition N2. For composition N1, the agglomerate sizes increase in spite of the further increase in the propellant burning rate and is apparently due to a decrease in the SL heterogeneity.

Pressure is also a factor contributing to changes in the properties of the products close to the burning-propellant surface. In addition, there are some reasons to suppose that not only the absolute values of parameters change, but the character of the CCP formation also changes with pressure. The only exception is composition N5 (Tables 3 and 4) for which the agglomerate fraction by mass in the flow remains approximately constant with increased pressure. Only the oxide content in the agglomerates increases. This increase with pressure is quite natural if one accounts for a need for increased amount of MF burning in the heterogeneous mode to ensure the transition to the gas-phase mode. For the other compositions, the pressure increase leads to a decrease in the agglomerate mass fraction in the flow. The extent of such a decrease grows as oxidizer specific surface increases. Similar effects also have been observed previously when burning propellants similar to the ones investigated in this study.[9,36] As these earlier experiments showed, these effects are concomitant with a rise in gas-phase temperature above the surface as one moves away from the burning-propellant surface and is evidence of metal burning in this zone.[37] Analysis of experimental data obtained in both the present and previous investigations supports the assumption that, as the pressure grows and metal particle size decreases, the probability increases that the transition from a heterogeneous mode to a gas-phase mode (Fig. 18) is nonstationary. The nonstationary effects consist of destruction of the particles by their gasification products because of the high rate of evaporation. These effects intensify the metal burning above the surface at distances from the surface less than the position of the sampling zone. For composition N5, these effects are not essential because of the
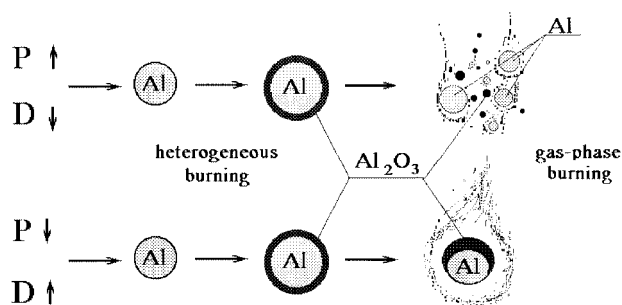
Fig. 18 Influence of pressure on combustion mode.

comparatively large size of the agglomerates, whereas for the other compositions they play an important role in CCP formation close to the burning-propellant surface.

In the process of agglomeration, three mechanisms might occur: pocket, prior-to-pocket, and interpocket types.[6,10] The first mechanism is characterized by the formation of only one agglomerate in each pocket and by the absence of dependence of agglomeration parameters on pressure. When the second mechanism occurs, the agglomerating particles leave the SL surface before the pocket burns out. The third mechanism supposes a possible fusion of particles belonging to different pockets (interpocket fusion). If the masses of the particles formed by these different mechanisms are comparable, then the density distribution function for the agglomerate size becomes polymodal. It was shown[6,10] that, for propellants having properties similar to those investigated here, but at close to atmospheric pressure, it quite probable that the pocket mechanism would dominate. Increasing the pressure increases agglomerate formation by the prior-to-pocket or interpocket mechanism. Thus, two factors are acting, one contributing to agglomerate size decrease, and the other to size increase. This competition between agglomeration mechanisms, as well as the nonstationary effects causing the small fraction to disappear, determines the agglomerate dispersity as a function of the pressure (Tables 3 and 4). The results obtained give another confirmation of the fact that the pressure might cause an increase, an absence of change, or a decrease in the agglomerate dispersity close to the propellant surface.

Formation of HDO

These studies show that the fine oxide particles are formed from the combustion of both the nonagglomerating and the agglomerating metal. (In the present paper, the metal particle formed by agglomerate fragmentation from nonstationary effects are included in the nonagglomerating-metal category.) Close to the burning-propellant surface, the combustion of the agglomerating metal is comparatively weak, which allows one to assume that the contribution from the nonagglomerating metal dominates HDO formation.

Note that the combustion mechanism for the highly dispersed metal particles was not studied in the presence of temperature, oxidation potential, and gas velocity fields. However, it is still possible to point out some quite obvious specific features of this process, namely, high rates of heat and mass exchange between the particles and their environment and potential contributions from nonstationary effects. It is unjustified to apply the laws of rather large-size particle combustion, for which quite a lot of experimental data have been obtained, to the situation examined here. It is quite probable that the combustion of the nonagglomerating metal occurs in two modes: heterogeneous and gas phase leading to CCPs being formed either on the burning-propellant surface or in the gas phase. The observed bimodality of the HDO particle size distribution density functions (Fig. 15) supports this assumption. One can suppose that the appearance of the small-size range is determined by the HDO formed in the gas phase, and the appearance of the large-size range is determined by the HDO formed on the metal particle surfaces by the heterogeneous mode. Because there is a higher probability that the small-size particles are missed in the sampling process compared to

the large-size particles, one can suppose that a large portion of lost particles (Table 5) are the small-size ones; that is, the fraction of particles formed by the first mode is somewhat higher than actually measured. Note that formation of oxide particles of sizes less than 100–150 mμm is a specific feature of processes taking place under the shock-wave stress condition seen with Al powder in which the appearance of similar particles is related to phenomena occurring in the gas phase.[38]

One can only suppose which parameters influence the combustion of metals that do not enter the agglomerates. Among them, one should include the propellant burning rate, the pressure, and the quantity of the particles participating in burning. The results of this investigation enable us to assert that the parameters characterizing the generation of the fine oxides close to the burning propellant surface are the individual characteristics of the propellant and its burning conditions. Note also that the sizes of the fine oxide particles found in this study, on average, are lower compared with the results from practically all of the previous works. (Remember that, in those studies, the final products of combustion were examined.) This observation allows one to assume that, in the process of evolving condensed products in the gas phase, when fine oxides are formed during the agglomerate metal burning, and the interaction of the carrier gas phase and the agglomerates[6,31] all take place, an increase in the sizes of the fine oxides can be expected.

Conclusions

In the process of the investigation, the following principal scientific results have been obtained:

1) General characteristics of the condensed-phase products of metals in solid propellants have been determined. It has been shown that these products consist of two essentially different types of particles: very fine particles and agglomerates. The morphological and chemical properties of these particles have been defined.

2) It has been shown that it is expedient to use concepts such as pocket and IPB when characterizing the propellant combustion-zone structure.

3) The effects of oxidizer particle size and combustion pressure on the proportions of agglomerates and fine oxide particles have been determined. An increase in oxidizer specific surface up to some level, which is determined by pocket formation conditions, decreases the fraction of metal participating in agglomeration. Further increases in oxidizer specific surface ensure an increase of this fraction. Combustion pressure is the factor that contributes to the agglomerate transformation relative to generation of fine oxides. Increasing pressure increases the agglomerate dispersity, which takes place close to the burning-propellant surface and therefore decreases the agglomerate fraction in the condensed products.

4) It was shown that the fraction of metal participating in agglomeration depends on the propellant combustion-zone structure. Knowing the characteristics of this structure allows one to predict the degree of metal agglomeration.

5) The influence of the oxidizer particle size on the agglomerate dispersity has been determined. This influence is manifest as a change in the propellant burning rate and pocket sizes. Increasing the rate and decreasing the pocket size decreases the agglomerate size.

6) It has been shown that the agglomerate formation may involve different mechanisms, which are called pocket, prior-to-pocket, and interpocket mechanisms. Changes in these mechanisms with pressure changes the character of pressure influence on the agglomerate size.

7) It has been established that the fine oxides are formed mainly in the burning of the metal that is not agglomerating. The fine oxide particle size distribution changes depending on both the pressure and the oxidizer particle size, that is, the individual characteristics of the propellant and combustion conditions.

The results obtained in this investigation are intended to improve mechanistic understanding of metal combustion in solid-propellant combustion and to contribute to the development of combustion theories for aluminized solid rocket propellants.

Acknowledgment

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