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Computer Model of Aluminum Agglomeration on Burning Surface of Composite Solid Propellant

Vishal Srinivas* and Satyanarayanan R. Chakravarthy†
Indian Institute of Technology Madras, Chennai 600036, India

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The process of agglomeration of aluminum particles on the burning surface of an ammonium perchlorate–based composite propellant is modeled using a computer algorithm. A random pack of particulate ingredients of given size and mass specifications is cast on the computer to simulate the propellant microstructure as reported previously. The aluminum particles are tracked as they emerge at a regressing burning surface, accumulate into filigrees, and get ignited by the near-surface leading-edge oxidizer–binder diffusion flamelets attached to the exposed areas of certain ammonium perchlorate particles. An approximate heat transfer model is incorporated to estimate the ignition delays radially inward and outward from the leading-edge flamelets into the filigrees accumulated over ammonium perchlorate particles and surrounding binder–fine ammonium perchlorate matrix layers. The delay influences the number of parent aluminum particles constituting a filigree, and consequently the size of the agglomerate that the filigree rolls up into. The implementation of the algorithm is validated against experimental results available in the literature, which were specifically obtained to investigate the relationship between the decrease in the agglomerate size and attachment of leading-edge flamelets over the fine ammonium perchlorate particles in the propellant with increase in pressure.

I. Introduction

ALUMINUM is an important ingredient in contemporary composite solid rocket propellants, not only from the viewpoint of energetics of the propellant formulation but also for providing the necessary damping of combustion instabilities that can potentially occur in the rocket motor. The damping is provided by the droplets of aluminum oxide that are produced by distributed combustion of what are referred to as aluminum agglomerates in the motor's combustion chamber. The product-oxide droplets would have to be within a specific size range for them to be able to effectively dampen a specific dominant frequency characterized by the natural acoustic modes of the chamber. Although the natural acoustic modes and the droplet size ranges required to dampen them can be estimated a priori in a motor development program, it is difficult to achieve the required product-oxide droplet size from the combustion of a given propellant formulation used in the rocket motor. Or conversely, it is difficult to design a propellant formulation, which upon combustion, would yield the product-oxide size distribution required for effective damping of acoustic oscillations in a specific motor. The difficulty is because of the fact that the aluminum particles embedded in the propellant undergo a complex set of processes that culminate in the formation of agglomerates, each of which contains a large number of parent aluminum particles. Because it is the agglomerates that undergo combustion to yield the product-oxide droplets, it is important to know how many parent aluminum particles typically constitute the agglomerates emerging from the burning surface of the propellant. Normally, this is not straightforward, because the accumulation and agglomeration of the parent aluminum particles on the burning surface of the propellant is not only affected by the aluminum size and content, but also directly depends on the other propellant formulation variables such as the total-solids loading, the mass fractions of the coarse and fine oxidizer particles and their size ranges, and so on, besides less directly on the type and amount of binder, ballistic modification, and the nature of the oxide coating on the aluminum particles.

The knowledge of the initial size distribution of the agglomerates emerging from the propellant burning surface is also important in simulating and predicting slag accumulation in the nozzle bucket of large rocket motors with nozzles submerged for thrust vectoring [1]. Numerical simulations of this problem typically assume a size distribution for the product-oxide droplets and march them toward the nozzle without simulating the combustion, or assume either an initial agglomerate size distribution and burn the agglomerates as they are convected in the combustion chamber. The latter effort has prompted in-depth analyses of the evolution, ignition, and combustion of metal particles/agglomerates in the recent past [2–4]. In any case, for the numerical simulation of the port flow, empirical inputs on either the initial agglomerate size distribution or the final product-oxide size distribution after combustion are required. Theoretical procedures for the prediction of the initial agglomerate size distribution for a given propellant formulation as a function of pressure are scarcely used for these purposes.

Grigoriev et al. [5] and Cohen [6] proposed the "pocket model" of aluminum agglomeration, by which the aluminum particles grouped together in the regions between adjacent coarse oxidizer particles tended to form agglomerates. This model brings in the effect of the overall propellant formulation to some extent in predicting the agglomerate size distribution. Kovalev [7] has partially adopted this model in the sense of examining the aluminum particles accumulated in a region on the burning surface of a propellant surrounded by coarse ammonium perchlorate (AP) particles, which is referred to as an elementary cell or a "flat pocket." He further considered a force balance on the agglomerates on the surface including gravitational and aerodynamic forces, and movement of particles along the surface because of a torque arising out of the aerodynamic force, and heating of the particles from the diffusion-kinetic flame between the oxidizer and the fuel. Jackson et al. [8] have recently adopted the idea of proximity of aluminum particles to each other in the propellant, in a manner similar to Cohen [6], but have applied it to computer-generated random packs of aluminum and AP particles representing the propellant microstructure. They have adopted two models of proximity, one in a spherical space around each aluminum particle, and another in a cylindrical space. These models involve one or two

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*Graduate Student, Department of Aerospace Engineering.
†Associate Professor, Department of Aerospace Engineering. Corresponding Author.

arbitrary parameters which are then calibrated for, by comparing the predicted size distribution with experimental observation.

Babuk et al. [9], while presenting carefully measured data on agglomerate size distribution at two pressures for five propellant formulations based on AP and isoprene rubber binder, also note the two concepts on the structure of aluminum agglomerates that are prevalent: one, in which the agglomerates are assumed to contain other ingredients, namely, the binder or its degradation products, and the oxidizer; the second, wherein the agglomerates are thought to consist only of metal and oxide drops. The second type is more prevalent in most propellants under most conditions. Babuk et al. [10] also refer to two classes of propellants ("mixed condensed systems"), one in which the ignition of the agglomerates occurs in the lower part of the surface layer, whereas in the other one, it occurs at the top. Babuk et al. [11] have also recently presented data on agglomerate size distributions for propellants containing energetic binders. In [9], it is pointed out that the agglomerate size generally decreases with increase in burning rate of the propellant, and that it also decreases with an increase in pressure; the latter could be because of the former, as the burning rate increases with an increase in pressure, in general. Several references are cited to observe that no trend is observed between the agglomerate size and pressure, regardless of the extent of the metal content in the propellant formulation.

The lack of any discernible trends noted above could be resolved by examining the proximity of the metal particles on the burning surface of a propellant to the flame structure in the gas phase combustion zone between decomposition products of AP and the binder. The work by Sambamurthi et al. [12] has qualitatively predicted trends in agglomerate size distributions based on the flame structure and validated these predictions on specific propellant formulations. This work was prefaced by experimentation with sandwiches with aluminum-filled binder versus dry-pressed pellets of AP and aluminum powders, wherein it was possible to infer the role of the near-surface leading-edge parts of the diffusion flamelets (LEFs) attached to the oxidizer/binder interfaces on the burning surface. Based on this understanding, a family of aluminized propellants with bimodal AP size distribution, with different fine AP sizes in different formulations of the family was formulated. These formulations were tested to confirm the prior expectation that there would be a fall in the agglomerate size distribution over a narrow pressure range for each formulation, and that this pressure range would shift to higher values if the fine AP size in the formulation is smaller. This is because it takes higher pressures for LEFs to be attached to smaller AP particles, which would bring the aluminum accumulated on the burning surface into greater proximity to more LEFs that act as their ignition sources. This would prevent further accumulation and cause a decrease in the average agglomerate size. These features are schematically depicted in Fig. 1. Price et al. [13,14] have also developed nonaluminized propellants to demonstrate jumps in their burning rates over narrow ranges of pressures which increase with decrease in the fine AP size in the propellants, because of LEF attachment over the fine AP particles with an increase in pressure. Price [15] has further elucidated the role of the LEFs in igniting the aluminum accumulates besides other important features of propellant combustion at typical rocket operating pressures.

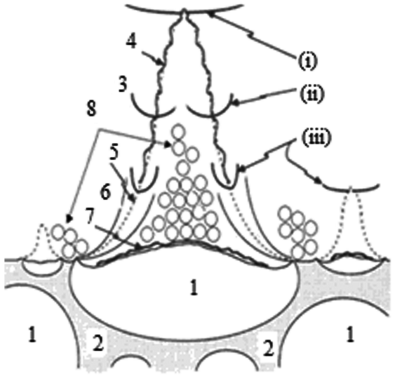


Fig. 1 Schematic of the flame complex and aluminum accumulation in the propellant combustion zone at different pressures (adapted from [13]). 1) AP; 2) binder; 3) leading-edge flame [LEF; i) at low pressure; ii) at intermediate pressure; iii) at high pressure]; 4) outer diffusion flame; 5) stoichiometric surface; 6) constant concentration surface in the mixing fan; 7) AP self-deflagration flame; 8) aluminum filigrees.

Price [16,17] has also discussed in great detail the fate of the aluminum particle embedded in the propellant microstructure as it emerges at the burning surface and eventually forms part of an agglomerate. As the particles emerge on the regressing burning surface, they accumulate there owing to their relatively greater thermal stability, but the aluminum tends to melt out of the particles' oxide skin by cracking the latter. Sintering of adjacent particles occurs, thus stringing a set of particles into a filigree. When a filigree comes in close proximity to an LEF over an AP particle of sufficient exposed area on the burning surface at the given pressure, it gets heated up and ignited. As the flame spreads across the particles in the filigree, the particles roll up into an agglomerate and leave the burning surface.

The above scenario forms the basis for a computer simulation of the agglomeration process in the present work. It represents the concept that the agglomerates primarily consist of aluminum and its oxide but not any of the other propellant ingredients, and is applicable to the more prevalent class of propellants in the classification scheme of Babuk et al. [9,10] wherein the aluminum filigrees accumulated on the burning surface get ignited from the side exposed to the combustion product gases. The objective of the simulation in the present work is to track all of the aluminum particles in the full propellant microstructure as the burning surface regresses at a given rate. By means of an algorithm detailed further below, the accumulation of the particles in filigrees on the burning surface is simulated, and the thermal delay of ignition of the filigrees in the vicinity of an LEF on an adjoining AP particle is estimated. The accumulation process continues until the thermal delay time elapses, upon which the aluminum particles in a given filigree are supposed to combine together to form an agglomerate. Thus, by burning a pack of propellant of a given formulation and collecting all the agglomerates emerging from the burning surface of the propellant pack, it is possible to estimate the agglomerate size distribution for that propellant composition. The key features of the present work are the following: 1) working with a random pack of particulate ingredients constituting the propellant microstructure, similar to Jackson et al. [8] instead of a statistically representative pocket inside [6] or at the burning surface of the propellant [7]; 2) attempting a physical construction of filigrees as they evolve on a regressing burning surface; 3) including the crucial presence of the LEFs on AP particles in the proximity of the accumulating filigrees; and 4) estimating the ignition delay for the filigrees to roll up into agglomerates and leave the surface during their thermal contact with an LEF. The last three aspects have not been taken into account in any of the past models of aluminum agglomeration.

The burning rate of the propellant pack is an empirical input to the present model. In practice, this information is readily available for most propellant formulations. The present work ignores the details of the oxide skin such as its thickness and composition, and consequently does not simulate the cracking up of the oxide skin or sintering between adjacent aluminum particles that come in contact with each other while accumulating. This could be crucial to the combustion stability behavior of rocket motors [18] and needs to be included in further refinements to the present work. Also, the nature of the binder and the movement of aluminum particles due to the flow of molten binder [19] and its irregular gasification [7] are not taken into account in the present agglomeration model. Additionally, the particles that come in mere physical contact with each other are specifically treated as belonging to a filigree that would eventually combine to form an agglomerate. Filigrees are always assumed to get ignited before leaving the surface, as mechanisms such as aerodynamic effects that lead to the filigrees leaving the surface before getting ignited have not been included in the present work.

The burning surface is also assumed to be flat, and any effect on the aluminum accumulation process that affects its agglomeration characteristics because of the nonplanar development of the burning surface is neglected in the present work. The assumption of a planar burning surface also implies that any ignition delays of AP particles and binder layers emerging on the burning surface are neglected, as they would be different at different parts of the surface at any instant, leading to nonplanarity. The heat conduction from the filigrees to the burning surface of the remainder of the propellant is also ignored in the present work, as it is observed that the burning rate of the propellant is not substantially altered by the presence of aluminum in general; this may, however, not be true with propellants containing ultrafine aluminum, reported recently [20].

II. Methodology

The present model is completely three dimensional in nature and is as close to reality as possible insofar as the simulation of the propellant composition is concerned. The computer model developed for this purpose involves the following steps:

1) Generation of the propellant cast given the propellant composition, by randomly packing all the AP and Al particles in a cuboidal space.

2) Determination of the flamelet distribution on the burning surface at any instant, for a given pressure.

3) Accumulation of aluminum particles as filigrees on the burning surface, as the latter regresses at an empirically inputted rate, keeping track of their proximity to the LEFs on the adjoining AP particles as determined in the previous step.

4) A heat transfer model to determine the time interval during which the aluminum accumulation proceeds without interruption while getting heated by the LEFs to ignite and form agglomerates.

5) Bookkeeping of the size distribution of the agglomerates as they leave the burning surface during the entire course of burning of the cast propellant pack, and verification of a global mass balance of the aluminum between the agglomerates and the particles originally present in the propellant.

A. Geometrical Modeling of the Composite Propellant Formulation

The formulation of a composite propellant is typically characterized by 1) total solids loading, 2) the mass fractions of the particulate ingredients constituting the solids, 3) the coarse-to-fine fraction ratio in the oxidizer particle size distribution, and 4) the particle size ranges of the oxidizer and other particulate matter in the propellant. This is besides the composition of the binder and other minor additives.

Sankaralingam and Chakravarthy [21] have presented a methodology to generate the microstructural detail of a cuboidal propellant cast of specified dimensions and composition on a computer. They have considered the four parameters listed above to specify the propellant formulation. The binder is considered to be homogeneous and it may also contain a very finely divided ballistic modifier additive; the latter is too fine to be packed as individual particles, and is hence considered as part of the binder, similar to how Chen et al. [22] treat the fine AP particles mixed in the binder. The particles considered for packing are assumed to be spherical.

B. Distribution of Flamelets Attached to Oxidizer Particles on the Burning Surface

Jackson and coworkers [23,24] have recently reported the simulation of combustion of composite propellants in the form of random packs of particulate ingredients including AP and Al in the binder. Such simulation would inherently identify AP particles that burn in an attached LEF versus those that burn in a premixed flame in different parts of the burning surface of the pack. However, to reduce the computational intensity, the fine AP particles are "homogenized" with the binder [22]. This poses limitations on what maximum size of fine AP can be regarded as acceptable for such homogenization. Specifically, if the goal is to determine whether the fine AP particles would have attached LEFs as the pressure is increased, then homogenization of the fine AP-binder blend is inappropriate. The approach of the present work requires the knowledge of the presence of attached LEFs on the different exposed surfaces of AP particles on the burning surface at any instant, so that they can be considered as sources of ignition of the aluminum filigrees in their vicinity after an appropriate delay. The present approach does not call for resolution of the actual structure of the LEFs on the different particles for the purpose of ignition of the aluminum filigrees. In this context, Price et al. [14] have described the criterion for flamelet attachment to AP particles on the composite solid propellant. In that reference, both order-of-magnitude estimates as well as rigorous expressions are evolved for the above criterion. But, in view of uncertainties over numerical values of thermophysical and chemical kinetic constants, the order-of-magnitude estimate seems to be closer to the experimental observations on pressure ranges of steep rises in burning rates for different fine AP sizes than that provided by the rigorous expressions. Accordingly, Sankaralingam and Chakravarthy [21] have applied the criterion based on the order-of-magnitude estimates to a three-dimensional computer model of a propellant cast for specific propellant compositions to determine those exposed areas of AP particles that burn with attached LEFs and those groups of particles that burn in a premixed flame at a given pressure. There are also some AP particles that are identified as not burning in either of these flamelets directly, but they may be merely pyrolyzing because of heat from the outer diffusion flame of a particle with an attached flame in the vicinity and/or burn in the AP monopropellant premixed flame, if the pressure is above the AP self-deflagration limit and if the exposed area of the AP particle is sufficiently large.

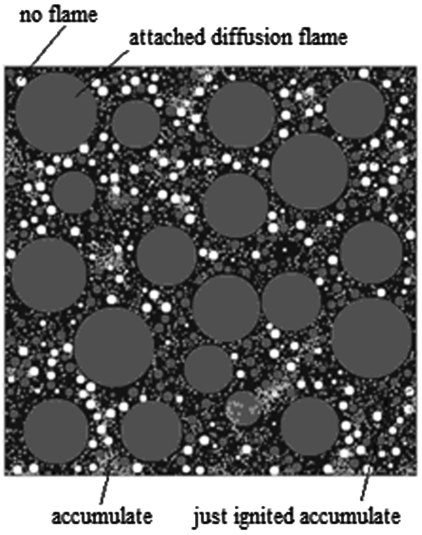


Fig. 2 Typical distribution of flamelet types on exposed areas of AP particles on the propellant burning surface (top view).

The present work follows the procedure evolved by Sankaralingam and Chakravarthy [21] for the prediction of the flamelet distribution on the burning surface of aluminized propellants at any instant, at a given pressure. The outcome of this procedure is depicted in Fig. 2, for a typical propellant cast whose formulation is given in Table 1, burning at 3.5 MPa. The figure shows the top view of the burning surface. It distinguishes the LEF-attached AP particles (dark gray circles) from those not burning directly in any oxidizer/fuel flame (white circles). The figure also shows accumulation and ignition of aluminum particles (light gray dots) on the burning surface, which is evolved in the manner described further below. The location marked as "just ignited accumulate" is space vacated by an aluminum accumulate after its ignition.

C. Accumulation of Aluminum Particles

The flamelet distribution on the burning surface described above is obtained at any arbitrary instant on a cut plane in a propellant pack that is representative of the burning surface. To accumulate aluminum that emerges from beneath the burning surface, the cut

Table 1 Composition of the typical propellant formulation

Type of particle	Mass fraction	Mean diameter, μm	Diameter range about the mean value	Truncation limit
Coarse AP	0.568	400	70	0.01
Fine AP	0.142	82.5	15	0.01
Al	0.180	15	0.001	0.01
Binder	0.110	——	——	——

plane representing the burning surface is traversed along the direction of overall flame propagation in the propellant at a rate inputted from experimental data for the given propellant formulation. The time is discretized into small intervals, during which the surface would regress by a distance smaller than the size of a typical aluminum particle. This is so as to ensure tracking of each of the aluminum particles as it emerges afresh on the burning surface. The gas phase flame complex is assumed to adapt quickly to the new surface features in terms of exposed areas of AP particles, and consequently, the flamelet distribution is worked out anew for each surface location in a quasisteady fashion.

As the burning surface regresses, the aluminum particles embedded in the binder are exposed. These aluminum particles are not ignited immediately but move along with the surface. If the aluminum particle encounters another aluminum particle from beneath, then it gets stuck to the one underneath, and a filigree of accumulated aluminum starts to form. Any binder layers present in between these particles are assumed to pyrolyze at the burning surface as the particles emerge out. As more and more aluminum particles get stuck to each other, the size of the filigree increases, as schematically depicted in Fig. 3. It is supposed here that once an aluminum particle comes in physical contact with another particle, sintering would take place, and the two particles in contact would form part of a filigree. The particles are not expected to nudge each other because gravity effects do not play a major role in the shaping of the filigrees. Besides, the sintering process, if it indeed occurs always as assumed here, ensures that a filigree can be in the form of a zigzag stack of aluminum particles. The particles are also assumed not to move laterally along the surface due to aerodynamic forces, as considered by Kovalev [7].

D. Ignition of Accumulated Filigrees: Heat Transfer Model

An aluminum filigree is heated mainly when it is within the proximity of an LEF attached to the periphery of an AP particle surface [12,15–17]. This is where the determination of the flamelet distribution on the burning surface at each instant during the surface regression assumes significance. In the present work, only those AP particle surfaces that are identified to have an LEF attached to them are considered for heating the aluminum filigrees accumulated in their vicinity.

Because aluminum is highly thermally stable, owing to its oxide skin, it takes some time for the filigrees to get heated to the point of ignition. Hence, it is important to estimate the ignition delay of the accumulating filigrees. The present approach is to develop a simple heat transfer model to estimate the ignition delay. Here, the simplicity in modeling the heat transfer is retained by treating it to be primarily a one-dimensional process.

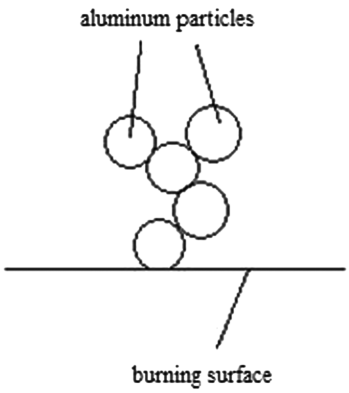


Fig. 3 Schematic depiction of filigree formation.

In attempting to model the ignition delay in such a simple manner, it is important to make a distinction between two possibilities. In one case, it is possible that the typical height of filigree accumulation is negligible when compared with the standoff distance of the LEFs that are heating the filigrees to ignition. In this case, the pyrolysis gases from the AP and binder layers beneath the accumulated filigrees would necessarily pass through the filigree bed to reach the flame, which implies that the convection of enthalpy by the gases would significantly alter the heat transfer from the flame to the filigrees than if such convection were to be ignored. On the other hand, in the other case where the typical height of the filigree accumulation is of the same order or greater than the LEF standoff distance, that is, if the filigrees are indeed protruding well into the gas phase flame, then the heating received by the filigrees from the flame would primarily be in a direction lateral to that of the convection of the pyrolysis gases and/or the gaseous combustion products. In this case, convection of enthalpy of the gas phase species through the filigree bed does not significantly influence the lateral heat transfer from the flame to the filigrees.

Figure 4 shows photographs of accumulating filigrees eventually leaving the surface as rolled up agglomerates at two different conditions, taken from [25]. It is clear from these photographs that the filigree accumulation is typically of a length scale of the same order or even much larger than the flame standoff distance. In view of this, an unsteady one-dimensional heat transfer model is developed in the present work wherein the heating from the flame to the filigrees is predominantly in the direction lateral to the flow of gases. At low pressures, the LEF standoff distance is high, but the extent of accumulation of the filigrees is also high; and at high pressure, the LEF standoff distance is low, and so the heat transfer to the filigrees is expected to be predominantly in the lateral direction across the pressure range of practical interest.

Again, two separate cases need to be considered: internal and external heating. The former is the heat transfer from the LEF/diffusion flame attached to an AP particle to those aluminum filigrees that are accumulated in the middle of the exposed surface of the AP particle. These filigrees appear in the middle of the AP particle surface as the AP particle emerges from beneath the burning surface when the accumulated filigrees move along with the surface from above. The additional heating from the AP self-deflagration flame, if present on the AP particle, is assumed to be negligible, following Sambamurthi et al. [12], as it also requires a two-dimensional treatment of the heat transfer. The latter, that is, the external heating, is the heat transfer from the LEF/diffusion flame attached to the AP particle, but in a radially outward direction, to those aluminum filigrees that are accumulated on the layers of the binder/fine AP matrix surrounding the AP particle with the attached flame. These two modes of heating are different because the internal heating involves a focusing of the heat toward the center, whereas the external heating involves dispersion of the heat over a region of increasing area. Accordingly, the ignition delay caused by internal heating is likely to be less than that caused by external heating, but not necessarily always so.

In the present work, the two modes of heating are dealt with separately, by constructing imaginary circular cylinders about an AP particle with the attached LEF for radial heating, inward or outward; see Fig. 5. The circular cylinders are considered to be made of porous

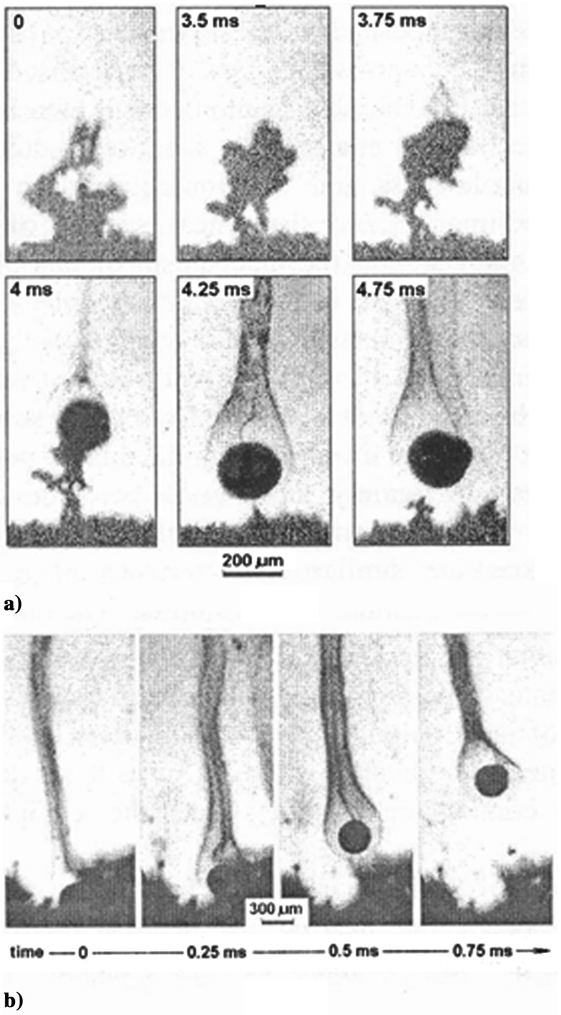


Fig. 4 Sequence of events in a) a "poor" agglomeration process, and b) a "ready" agglomeration process [25].

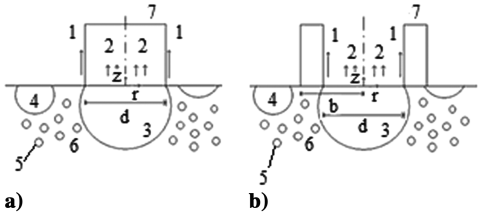


Fig. 5 Schematic representation of a) internal heating, and b) external heating of equivalent circular cylinders of porous aluminum representative of the accumulated filigrees in their respective regions. 1) flame at temperature "T_f"; 2) hot gases rising from surface; 3) coarse AP; 4) fine AP; 5) aluminum; 6) binder; 7) cylinder of porous aluminum rod [in a) inner cylinder, in b) outer cylinder]; *d* represents the exposed diameter of a coarse AP/outer diameter of an inner cylinder/inner diameter of the outer cylinder; *b* represents the outer diameter of the outer cylinder.

aluminum, with uniform porosity that is calculated based on the actual number and precise location of the individual aluminum particles constituting all the filigrees with the regions that the cylinders are considered to encompass. The inner cylinder, considered for the internal heating, is taken to have the same diameter as that of the exposed area of the AP particle with the attached LEF. This assumes that the LEFs are more or less attached to the peripheries of the exposed AP on the burning surface, when in reality, it could be attached over the surface of the AP particle, that is, within its periphery, or on the binder side, that is, outside the particle periphery, if a sufficient amount of fine AP particles are present in the binder without any LEFs attached to them. This detail has been ignored in the present work. The outer cylinder, considered for the external heating, is hollow, with the inner diameter equal to that of the exposed area of the AP particle on the burning surface, and the outer diameter taken to be that distance where an accumulated aluminum filigree or particle would be within the thermal influence of the flame. In the present work, the outer diameter of the outer cylinder is taken to be greater than its inner diameter by 100 μm. Although a semi-infinite hollow cylinder, that is, one with infinite outer diameter, could be analytically treated, to mathematically determine the region of thermal influence, the above limit has been computationally set for the outer diameter for the purpose of calculating the porosity of the outer cylinder. As the aluminum accumulation is expected to occur everywhere on the burning surface, the porosity would not be affected considerably by the choice of the above value.

The transient one-dimensional equation for radial heat conduction is

$$\frac{1}{\alpha}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} \tag{1}$$

subject to the boundary condition for the internal heating problem as

$$\left.\frac{\partial \theta}{\partial r}\right|_{r=0} = 0 \quad \text{and} \quad \left.\left(\frac{\partial \theta}{\partial r} + H_{\text{int}}\theta\right)\right|_{r=a} = 0 \tag{2}$$

and the initial condition $T(r,0) = T_s$. Here, α is the thermal diffusivity of the porous aluminum, $\theta = T - T_f$, where T_f is the flame temperature in the LEF and its trailing outer diffusion flame (taken to be approximately uniform), T_s is the surface temperature at which the aluminum particles emerge above the burning surface and form part of the filigree, $H_{\text{int}} = h/k_{\text{int}}$, where h is the convective heat transfer coefficient, and k_{int} is the thermal conductivity of the porous aluminum in the inner cylinder; $a = d/2$. The thermophysical properties such as α and k_{int} are calculated as the average of the respective properties of aluminum and the combustion product gases, weighted by the porosity in the cylinder, which is calculated based on the filigree formation detailed in the previous subsection. The solution to Eq. (1), with the above boundary and initial conditions, gives the expression for the time delay to attain a certain ignition temperature T_i in the inner cylinder, as

$$\tau_{\text{int}} = \frac{1}{\alpha\beta^2}\ln\left\{2\frac{H_{\text{int}}}{a}\left(\frac{T_f - T_s}{T_f - T_i}\right)\frac{1}{(H_{\text{int}}^2 + \beta^2)}\right\} \tag{3}$$

where β is the first positive root of the equation [26]

$$\beta J_1(\beta a) - H_{\text{int}} J_0(\beta a) = 0 \tag{4}$$

with $J_0(x)$ and $J_1(x)$ being the Bessel's functions of order zero and one, respectively.

For the external heating in the outer cylinder, the governing equation is the same as Eq. (1), with the same initial condition as in the internal heating problem, but the boundary conditions are

$$\left.\left(\frac{\partial \theta}{\partial r} + H_{\text{ext}}\theta\right)\right|_{r=a} = 0 \quad \text{and} \quad \left.\frac{\partial \theta}{\partial r}\right|_{r=b} = 0 \tag{5}$$

where $H_{\text{ext}} = h/k_{\text{ext}}$, with k_{ext} being the thermal conductivity of the porous outer cylinder. In this case, the time delay t_{ext} to attain the ignition temperature T_i in the outer cylinder is given by the implicit expression

$$\exp(H_{\text{ext}}^2 \alpha \tau_{\text{ext}})[1 - \text{erf}(H_{\text{ext}}\sqrt{\alpha\tau_{\text{ext}}})] = \frac{T_f - T_i}{T_f - T_s} \tag{6}$$

Equations (3) and (6) are evaluated using the following numerical values for the different thermal and thermophysical properties: $h = 5\ \text{W} \cdot \text{cm}^{-2} \cdot \text{K}^{-1}$ [26], and $T_i = 2320$ K. Other pertinent values are taken from [14]. The choice of value for the ignition temperature

corresponds to the melting point of Al_2O_3, signifying that when the oxide skin on the aluminum particles in the filigree begins to melt, then the aluminum metal within is exposed for further heating so that vaporization of the metal and consequently gas phase oxidation, that is, combustion, may occur, which marks the ignition.

The key role of the ignition delay, either during internal or external heating, is that it allows for the accumulation of aluminum particles in a filigree to proceed until ignition occurs. This has a significant effect on the size distribution of the agglomerates emerging from the propellant burning surface, as will be shown in the next section. Furthermore, it is also likely that during the ignition delay, the burning surface topology changes such that a set of filigrees moves out of the thermal influence of the LEF/diffusion flame attached to the AP particle in their vicinity. This would occur when the exposed area of the AP particle on the burning surface shrinks to such an extent that the LEF detaches from the remainder of the particle. In such a situation, the filigrees that were being heated hitherto by the flame would start to cool down. Heating would resume when they gain proximity to another LEF attached to another particle in their vicinity, but the initial temperature is no longer T_s, but a value to which the filigree had cooled down before the heating resumed. Further, during the time of cooling and reheating, these filigrees would also have accumulated more aluminum particles, which in turn affects the size of the agglomerates that those filigrees roll up into. These features have been included in the present work.

The effect of an increase in pressure on the agglomerate size distribution is in causing more LEFs to be attached to the exposed AP surfaces, thereby providing greater proximity for the accumulating aluminum filigrees to newer sources of heat and ignition in these LEFs. This arrests the accumulation process more often, leading to smaller agglomerates leaving the burning surface. The effect of an increase in pressure by greater heat transfer to the aluminum filigrees through the decrease in the LEF standoff distance requires a two-dimensional heat transfer model, which is not adopted in the present work, although the standoff distance is estimated in evaluating the criterion for the LEF attachment.

E. Agglomerate Formation

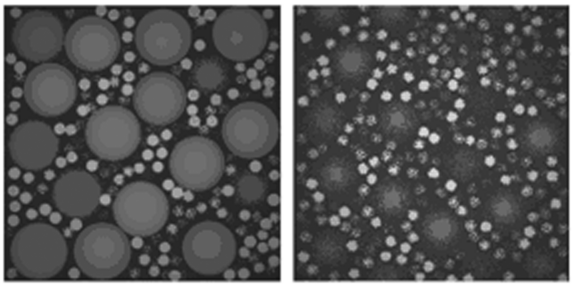
Once a set of filigrees within the thermal influence of an LEF gets ignited, the individual filigrees roll up into agglomerates almost instantaneously because of the rapid spread of the aluminum flame from the point of ignition. The size of the agglomerate rolling up from any filigree is calculated by assuming the agglomerate to be spherical, and equating its mass to the sum of the masses of the individual aluminum particles making up that filigree.

A large number of agglomerates are thus formed as the burning surface traverses a typical propellant pack of given formulation, with many sets of filigrees getting ignited by LEFs attached on the exposed AP surfaces across the burning surface at different instants of time during the traverse. The size distribution of all the agglomerates thus collected is the end result of the present exercise. Thus, the essential feature of the entire exercise is proper book-keeping of all the aluminum particles, their filigrees, and the sizes of the agglomerates that the filigrees roll up into after appropriate ignition delays.

Finally, an overall mass balance is verified by comparing the sum of the masses of all the aluminum agglomerates leaving the surface with the total mass of aluminum originally present in the unburned propellant pack as individual particles. A good comparison of the two quantities within a small error is an indicator of the successful implementation of the above methodology.

III. Results and Discussion

In this section, first a typical formulation is considered to illustrate the implementation of the above methodology in a step-by-step fashion and to examine certain specific features such as the role of ignition delay in determining the agglomerate size distribution. In the next part of this section, we consider the family of propellant formulations experimentally tested by Sambamurthi et al. [12] and apply the methodology developed here to those formulations to compare its predictions with experimental results. The experimental results of [12] have been chosen here for comparison because the propellant formulations tested in that work were specifically developed to examine the effect of the attachment of LEFs over fine AP particles on the size of aluminum agglomerates; and, the present work phenomenologically models this aspect.



a) b)

Fig. 6 a) Elevation and b) plan view of computer-cast propellant pack of the typical formulation given in Table 1.

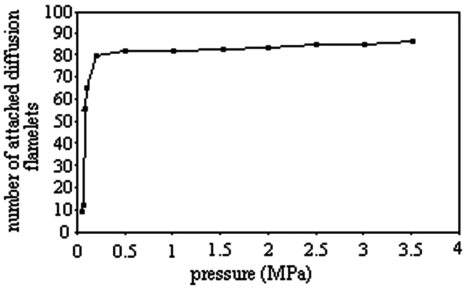


Fig. 7 Flamelet distribution for the typical propellant formulation.

A. Typical Propellant Formulation

1. Cast Generation

Table 1 shows the typical formulation under consideration. This formulation is used to cast a propellant pack of cubical dimensions of 5 times the mean diameter of the coarse AP particles on a computer. The plan and elevation of the cast propellant pack is shown in Fig. 6.

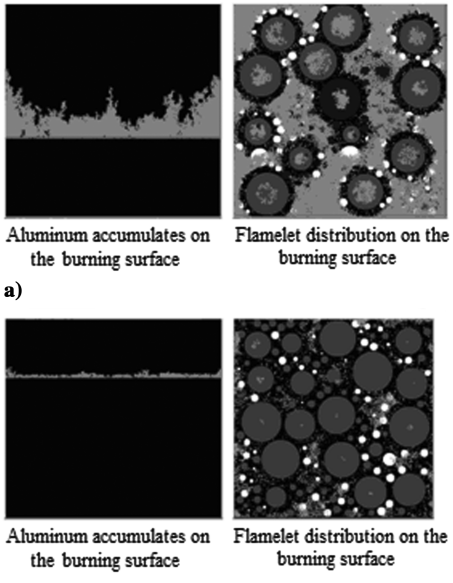


Fig. 8 Plan and elevation views of aluminum accumulation at two pressures: a) 0.04 MPa, b) 3.5 MPa.

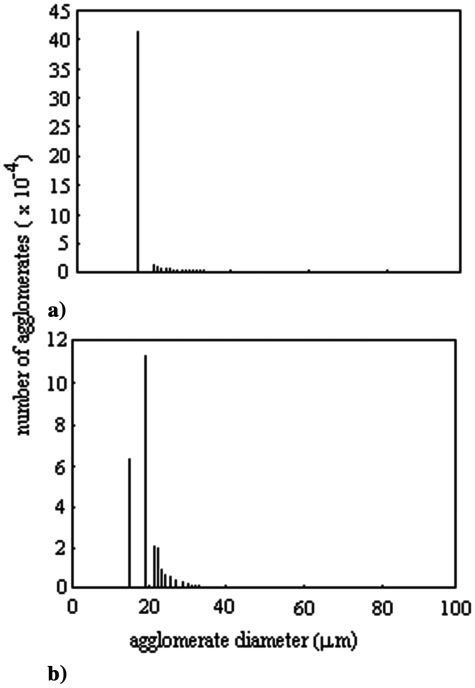


Fig. 9 Agglomerate size distribution for the propellant formulation in Table 1 at a pressure of 0.1 MPa for two values of ignition delay: a) 1 ms, b) 2 ms.

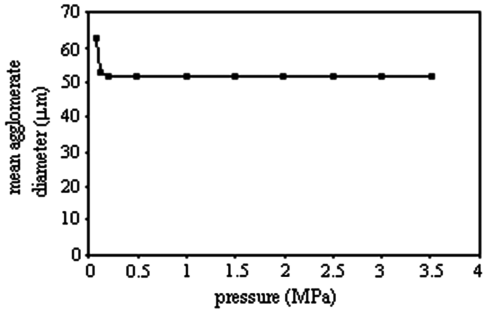


Fig. 10 Variation of mean agglomerate size with pressure for the formulation given in Table 1.

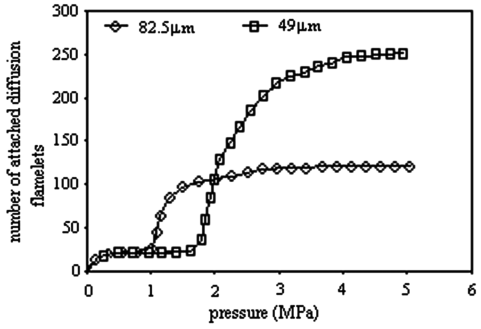


Fig. 11 Number of AP particles with attached diffusion flamelets as a function of pressure for propellant formulations in Table 2.

2. Flamelet Distribution

The flamelet distribution on an arbitrary cut plane representing the burning surface on the computer-cast propellant pack of the typical formulation above is predicted following Sankaralingam and Chakravarthy [21] (shown in Fig. 2). The numerical values of all the relevant parameters are the same as in [14]. Figure 7 shows the number of AP particles exposed on the burning surface that burn in attached LEFs, as a function of pressure for this propellant. It can be seen that the number of particles with LEFs attached greatly increases in a narrow range of pressure. It is not possible to be sure if the above pressure range is valid in reality unlike the validation done in [20], but for the purpose of examining the present typical formulation, it is important to note the sharp rise in number of LEF-attached particles.

3. Aluminum Accumulation

As the burning surface regresses through the propellant pack, the aluminum particles accumulate into filigrees on the burning surface. For the purpose of understanding the accumulation process, an artificial delay time of 1 ms is considered during the heating of the filigrees within a thermal influence zone of 50 μm on the inside and outside from the peripheries of the AP particles with attached LEFs on the burning surface at any instant as determined above, without applying the heat transfer model detailed earlier to estimate the ignition delays. In this case, the scenario of aluminum accumulation is shown in Fig. 8 at two different pressures on either side of the jump in the number of LEF-attached AP particles. It can be seen that when the number of LEF-attached particles is low, the aluminum

Table 2 Composition of unaluminized propellants [14]

Formulation no.	Type of particle	Mass fraction	Mean diameter, μm	Diameter range about the mean value	Truncation limit
1	Coarse AP	0.7	400	70	0.01
	Fine AP	0.175	82.5	7.5	0.01
2	Coarse AP	0.7	400	70	0.01
	Fine AP	0.175	49	15	0.01

Table 3 Composition of experimental aluminized propellants [12]

Formulation no.	Type of particle	Mass fraction	Mean diameter, μm	Diameter range about the mean value	Truncation limit
1	Coarse AP	0.568	390	70	0.01
	Fine AP	0.142	49	9	0.01
	Al	0.180	30	0.001	0.01
2	Coarse AP	0.568	390	70	0.01
	Fine AP	0.142	82.5	15	0.01
	Al	0.180	30	0.001	0.01
3	Coarse AP	0.568	390	70	0.01
	Fine AP	0.142	196	32	0.01
	Al	0.180	30	0.001	0.01

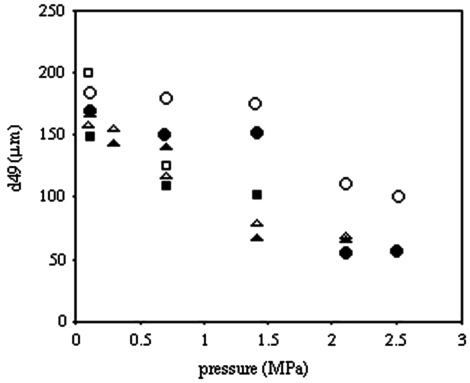


Fig. 12 Comparison of predicted and experimental agglomerate sizes for propellant formulations in Table 3. Open symbols: experiment [12]; filled symbols: prediction. Circles: 49 μm; triangles: 82.5 μm; squares: 196 μm.

accumulation closely resembles the initial instants of the "poor" agglomeration process in the photographs of propellant combustion shown in Fig. 4.

4. Ignition Delay

It is interesting to examine the role of ignition delay, even if artificially, on the agglomerate size distribution. Figure 9 compares the size distribution of the agglomerates obtained at a pressure of 1 bar for an artificial ignition delay of 1 and 2 ms, without incorporating the heat transfer model. With 1 ms, most of the individual aluminum particles leave the surface without appreciably accumulating into filigrees, so that the dominant size is the parent aluminum particle size; whereas, a shift in the dominant size of agglomerates is observed when the ignition delay is increased to 2 ms, because of the greater opportunity for the aluminum particles to accumulate as filigrees.

5. Variation of Agglomerate Size with Pressure

With the ignition delay retained as 1 ms, as in Fig. 8, the mean agglomerate diameter is plotted as a function of pressure in Fig. 10, for the typical formulation considered here. It can be seen that there is a marked fall in the agglomerate size in the same pressure range as where there is a marked rise in the number of LEF-attached particles on the burning surface. This confirms the role played by the LEFs in heating and igniting the aluminum particles accumulated on the burning surface, as suggested by Sambamurthi et al. [12] and Price [15–17].

B. Comparison with Experimental Data

It is important to ensure that the jump in the number of LEF-attached AP particles on the burning surface is verified in some way by experiments, before proceeding to compare the predicted agglomerate sizes with experimental data. Sankaralingam and Chakravarthy [21] have shown these jumps for a family of nonaluminized propellants with different fine AP sizes whose burning rates also exhibited similar jumps in narrow pressure ranges. However, although they could capture the trend of finer AP showing the jump at a higher pressure, the actual pressure ranges were underpredicted. This has necessitated revisiting that work as part of the present studies. It has been possible to slightly adjust the numerical value of the preexponential factor in the Arrhenius expression for the reaction rate of the gas phase premixed flame and obtain the jumps in the number of LEF-attached AP particles to coincide with those in the burning rates of the nonaluminized propellants. This is shown in Fig. 11; the compositions of the corresponding nonaluminized propellant formulations are listed in Table 2. The revised value of the preexponential factor is 3×10^{11} g $\cdot$ cm^{-3} and 2.5×10^{10} g $\cdot$ cm^{-3} at an oxidizer/fuel ratio of 0.77 and 0.84, respectively.

The revised values of the preexponential factor are now used for the purpose of prediction of the aluminum agglomeration. The family of aluminized propellant formulations considered for this purpose is taken from Sambamurthi et al. [12] and their compositions are shown in Table 3. These formulations are computer cast into propellant packs and the aluminum agglomerate size distribution for each of them is obtained at several test pressures. The weighted mean diameter d_{49}, computed in the same manner as Sambamurthi et al. [12], is obtained for each of the size distributions at all the test pressures. The predicted d_{49} is compared with the experimental results in Fig. 12. It can be seen that the agreement is good mainly in the pressure range of the drop in the agglomerate size for each formulation, corresponding to the increase in the number of LEF-attached AP particles on the burning surface. For the case of 49 μm fine AP size, there is a uniform downward shift in the predicted values relative to the experimental data at all pressures. This points to the need to test the formulation with still finer AP size (17.5 μm) for which experimental data are available [12]. That formulation has not been tested in the present study because it requires a large computational time to cast the propellant pack, as it involves a large number of fine AP particles. Testing it would reveal if the disparity between the predicted and observed results widens with the use of finer AP particles.

IV. Conclusions

The present work models the agglomeration process of aluminum particles in the combustion zone of AP-based composite solid propellants in a phenomenological manner. Two key aspects of the modeling are the consideration of the AP particles with exposed areas on the burning surface with an LEF attached and the inward and outward ignition delays for the aluminum filigrees getting heated in the LEF-outer diffusion flame complex. These two aspects have made it possible to show the link between the attachment of LEFs on AP particles with an increase in pressure and a corresponding decrease in the aluminum agglomerate size, and the effect of ignition delay in determining the agglomerate size distribution. In view of the latter, the role of the heat transfer model is imperative.

Several further refinements to the present model are possible. In principle, simulation of the heating up of the insides of each and every aluminum particle from a three-dimensionally and temporally resolved flame structure and accurate modeling of the filigree formation are required, but these may be too difficult to carry out in the near future. The role of the oxide skin on the parent aluminum particles in the filigree formation and ignition delay, and consequently on the agglomerate size distribution, may, however, be important from a practical standpoint. Interest in plateau burning propellants involving flow of molten binder on the burning surface also necessitates consideration of lateral movement of aluminum particles along the surface during the agglomeration process.

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S. Son
Associate Editor