JOURNAL OF PROPULSION AND POWER
Vol. 27, No. 3, May–June 2011

Reduced Agglomeration of Aluminum in Wide-Distribution Composite Propellants

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DOI: 10.2514/1.50127

Aluminum behavior (accumulation, agglomeration and ignition) is studied in a unique, wide-distribution, ammonium perchlorate/hydroxyl-terminated polybutadiene propellant formulation that results in low Al agglomeration, even at low pressures (1–30 atm). A fuel-rich, physically oxygenated binder matrix highly loaded with very fine ammonium perchlorate at a high fine ammonium perchlorate/binder ratio is found to have premixed flame conditions that produce minimal agglomeration (without ignition) of Al. Coarse ammonium perchlorate is added to the system in the form of either particles or pressed-ammonium perchlorate laminates (simulated coarse ammonium perchlorate). Both laminate and particulate systems show that with coarse ammonium perchlorate present, Al can agglomerate on coarse ammonium perchlorate via lateral surface migration from fuel matrix to the coarse ammonium perchlorate region. The particulate coarse ammonium perchlorate system also shows that Al can accumulate/agglomerate via settling on coarse ammonium perchlorate from above (in the direction of burning). Both systems show that with coarse ammonium perchlorate present, Al is ignited by the outer coarse ammonium perchlorate/fuel matrix canopy flames, which the laminates clearly show to be either split-diffusion or merged-partially-premixed, depending on pressure and diffusion length scale (fuel layer thickness). Thus a propellant formulation is proposed for reducing overall Al agglomeration through intrinsically reduced agglomeration in the fuel matrix and a reduced number of coarse ammonium perchlorate-particle agglomerates via higher fine ammonium perchlorate/coarse ammonium perchlorate ratio.

I. Introduction

ALUMINUM behavior (accumulation, agglomeration, and ignition) on the surface of composite propellants [ammonium perchlorate/hydrocarbon-binder (AP/HC)] has been studied but a complete understanding is still lacking, and as a result undesirable aluminum agglomeration has been difficult to predict and control. The inclusion of aluminum in a composite (heterogeneous) propellant adds complexity to an already complex combustion system. Composite propellant flames (AP/HC) are intrinsically three-dimensional and unsteady, even when the macroscopic environment (e.g., pressure) is fairly steady. Understanding the combustion of a nonaluminized composite propellant is a serious challenge, even without the added complication of aluminum agglomeration; and yet it is crucial to understand the former in order to understand and be able to control the latter, since the non-Al flame environment plays such a strong role in determining Al behavior.

One of the most useful tools in elucidating AP/HC flame structure has been the two-dimensional laminate propellant. The primary advantage of the laminate propellant is that one of the flames of the AP/HC system, that between coarse ammonium perchlorate (CAP) oxidizer and fuel-binder, is made essentially two-dimensional and steady, instead of three-dimensional and unsteady, by replacing particulate CAP with slabs or laminae. Several investigators have made extensive use of the laminate system to clarify surface behavior [1,2] flame behavior [3], and combined flame-surface behavior [4–6]. It is natural to make use of this geometrically simplified system to study the combustion of Al, specifically its agglomeration and ignition behavior.

This paper presents an experimental study of aluminum behavior in wide-distribution, bimodal ammonium perchlorate hydroxyl-terminated polybutadiene (AP/HTPB)-binder propellants using a variety of propellant configurations, including laminates and nonlaminates. We describe the discovery of a propellant formulation with significantly reduced overall Al agglomeration. Both Al behavior and non-Al propellant surface/flame structure are examined, and their crucial interaction is further clarified. A hierarchy of propellant architectures is used, from relatively "simple" fuel-rich, quasi-homogeneous, one-dimensional binder-matrices, to two-dimensional, quasisteady AP/HTPB/Al laminates, to full three-dimensional, unsteady bimodal particulate AP/HTPB/Al composite propellants. The latter confirm the aluminum mechanisms observed in the one-dimensional and two-dimensional systems, including those thought to be most relevant in the new, reduced-agglomeration formulation.

II. Background

Two things primarily influence agglomeration and ignition: AP/HC-binder flame conditions and propellant microstructural geometry. A composite propellant (Fig. 1) containing a mixture of HC-binder (fuel), fine ammonium perchlorate (FAP), and aluminum (typically ranging from 16–18% by mass) is packed between CAP particles (e.g., 200–400 μm) forming a "pocket." (A pocket is the region between CAP; this region is also referred to as the FAP/fuel matrix.) The aluminum pocket geometry effect was addressed in papers by Grigoriev et al. [7] and Cohen [8]. The model estimates the fraction of parent aluminum powder that will agglomerate on a composite propellant surface by focusing on pocket conditions including particle size, composition, and effective volume. An "effective pocket" is defined corresponding to the size of the ammonium perchlorate (AP) particles that "bound" or form the edges of the pocket. In a bimodal particulate propellant, CAP particles form pockets that contains aluminum, binder, and FAP particles, which themselves form smaller pockets of aluminum and binder. According to the pocket model, the fraction of aluminum that melts will coalesce into an agglomerate with a diameter generally the size of the pocket.

In addition to pocket geometry AP/HC-binder flame conditions also greatly influence aluminum behavior. An AP/HC-binder flame

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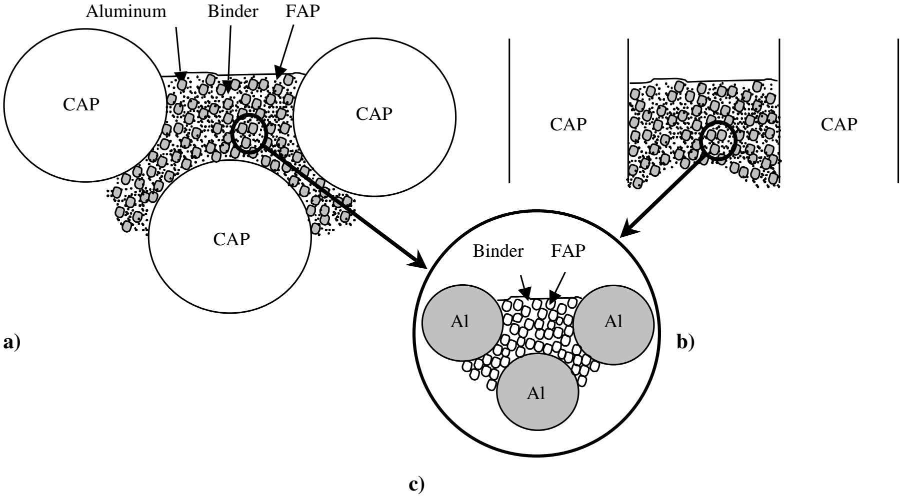


Fig. 1 Schematic representation of propellant formulations: a) three-dimensional particulate propellant with wide-distribution FAP (2 μm) and CAP (200 or 400 μm) particles, (b) two-dimensional laminate propellant with CAP particles replaced by CAP lamina, and (c) one-dimensional oxygenated binder with Al (15 μm).

can be either diffusion or premixed, depending on particle Peclet number (Pe), with flame temperatures ranging 1600–2900 K. Each flame type, when considered separately, can be observed and its impact on agglomeration and ignition determined. The premixed mode occurs for $Pe \ll 1$ (lower pressure and smaller AP size). As Pe increases toward unity the gas flames become less premixed. For $Pe \gg 1$ (higher pressure and larger AP size) diffusion flames having partially premixed leading-edge flames (LEF) form near AP/binder interfaces.

In the present study, wide-distribution bimodal AP is used with 2-μm FAP and either CAP particles (200 or 400 μm) or simulated "CAP" laminates of pressed AP. The FAP is sufficiently small that the one-dimensional quasi-homogeneous, fuel-rich FAP/binder matrix burns in the premixed mode. The CAP particles or lamina are large enough that the oxy-fuel matrix/CAP system burns in the diffusion flame mode if the fuel region length scale is sufficiently large to achieve $Pe \gg 1$. How large is large enough depends on pressure and is discussed further next. Each subsystem, a) pure matrix without CAP and b) wide/thick matrix with CAP, represents an opposite limit of the general bimodal-AP/HC propellant system, and is therefore a useful way to study the interaction between AP/HC flame structure and Al behavior.

The behavior of aluminum in AP/HC propellants also depends on its thermophysical properties and those of the binder system in which it is embedded. Aluminum powders have a relatively low melting point (930 K), which is comparable to the surface temperatures of burning propellants. Typical binders, such as HTPB, form a thin melt layer on the burning surface to which the aluminum can cling. As the propellant surface regresses, the aluminum particles in the binder melt remain unignited and begin to concentrate on the surface. Although they are able to move around in this thin melt layer, typically the surface tension of the melt serves to retain the aluminum. As a result, parent aluminum powder accumulates on the burning surface of the propellant, melts, and coalesces or agglomerates to form larger particles that eventually separate from the surface.

Past studies have seen a focus on trying to understand the physics behind aluminum agglomeration, ignition, and detachment from the surface and have shown that typical propellant formulations result in Al agglomerates that are several hundred micrometers in diameter. A brief, general summary of these processes applied to an AP/HC follows [9–12]. Surface temperatures are lower than the aluminum oxide melting point so the aluminum will not ignite on the surface of the propellant. By processes still not fully understood, neighboring aluminum particles on the surface begin to coalesce together to form larger clumps of aluminum referred to as accumulates. At this stage, the accumulates have an ill-defined shape and are typically not spherical. The accumulates can continue to migrate around the surface, ignite, and/or detach from the surface or they can form chain extending into the gas phase called filigrees. Sooner or later the accumulates or filigrees are exposed to high temperatures (>2300 K) in the flame near the surface, causing the protective oxide layer of the protruding accumulate or filigree to melt, exposing the aluminum inside to the oxidizing environment. A rapid series of oxidizing reactions occurs, intense heat is given off, spherical droplets also known as agglomerates form from the chains of individual particles, and ignition occurs. If not already separated from the surface, the rapid rise in temperature due to the oxidation reactions increases the drag forces and propels the agglomerates away from the surface and into the flowfield. Aluminum combustion continues as the agglomerate droplets flow in the hot gases above the propellant surface. Conventional propellant formulations have a CAP/FAP ratio and FAP sizes that can not support a premixed flame in the FAP/fuel matrix [12]. Ignition of aluminum agglomerates occurs either on or above the propellant surface. Flame temperatures [13] near the aluminum oxide melting point of 2300 K, are generally required to melt the agglomerate's protective oxide coating and induce ignition. The majority of aluminum combustion takes place in the flowfield, away from the burning surface, with some residual aluminum possibly exiting the system unburned. Complete aluminum combustion internal to the system is preferred as unburned aluminum does not contribute to specific impulse and has both thermal and momentum two-phase flow losses. In this regard, less extensive agglomeration is better for system performance. Using the D^2 model correlation developed by Beckstead [14] from his fit to collected data for a 300-μm Al agglomerate burning at 68 atm (6.9 MPa), the burnout time is approximately 255 ms. (Pressures at this level have little to no effect on burnout time [15].) If the residence time is not longer than that, as it might not be in a small motor or even in a large motor if the agglomerate originated at the aft end, a portion of the droplet's energy release will not be realized by the system.

In recent years there has been interest in the possibility of using nanoaluminum to improve propellant combustion characteristics, primarily to increase propellant burning rate [16,17]. While the several-fold increases in burning rate that were anticipated have not been realized, in some cases (e.g., when CAP is very coarse) nanoaluminum has been seen to increase burning rate by a factor of 2. No significant reduction in agglomeration with nanoaluminum has been reported, but it may be important to note that other than decreasing Al size the rest of the propellant formulation has remained conventional (e.g., FAP/binder ratio).

There have also been several efforts to develop mathematical or computational models to simulate and predict aluminum agglomeration behavior beyond the pocket model [18,19]. Kovalev

[18] included, among other things, consideration of drag forces on the agglomerates at the surface and heating by LEFs of the AP/HC diffusion flames. Some studies [19] have shown the ability to match trends between AP/binder flame structure (e.g., LEF presence or absence) and agglomerate size. However, none of the models have considered wide-distribution propellants with the high FAP/binder ratio considered here. Furthermore, the extent of formulation parameter space over which simulation has been tested is rather limited. It must be said that presently available codes and models still have not demonstrated the ability to predict, from first principles, aluminum agglomeration over a wide formulation parameter space. Yet, without fundamental understanding of all areas of combusting propellant behavior on a microscopic level, no computer code will be able to simulate accurate and validated heterogeneous propellant combustion. More experimental data under more controlled propellant conditions are required; in this regard the wide-distribution, high FAP/binder ratio propellant offers a unique opportunity to challenge present thinking and further develop simulation capability.

The strategy employed here is to isolate and/or simplify the various flame zones in the complex AP/HC flame system. There are basically two AP/HC flame zones that can be isolated: a) the inner premixed flame of the FAP/binder (matrix) and b) the outer, canopy flame between CAP (particles or lamina) and the fuel-rich matrix, which, as noted, can be either split (diffusion) or merged (partially premixed). The influence of the inner, matrix flame on Al behavior is studied by simply isolating the aluminized fuel-rich, pocket-propellant matrix. The outer CAP/fuel flame is isolated and studied by making two-dimensional laminate propellants. This changes the intrinsically three-dimensional, unsteady flames of particulate, composite propellants into two-dimensional, quasi-steady flames in laminates by replacing CAP particles with CAP laminates. The fuel-rich matrix is placed between layers of AP to form a laminate sandwich. In laminates, the flowfield (minus aluminum) is closer to being steady than in particulate propellants, and the outer diffusion flames are also steadier with a well-characterized two-dimensional geometry. AP/HTPB-binder flames in both pure-binder and oxygenated-binder laminate propellants have been studied in the past and flame regimes delineated, as noted next [6]. The objective here is to study aluminum behavior by adding aluminum powder to the oxygenated fuel region of the high FAP/binder ratio, small FAP-size, laminate propellants. The influence of propellant composition variables such as diffusion length scale (fuel layer thickness) on the propellant surface structure, flame characteristics, and behavior of aluminum can thus be studied as well as the effect of pressure or other motor environmental parameters.

III. Experimental Approach

The overall approach taken for this work was to vary the dimensional complexity of the propellant system by transitioning between monomodal-AP and bimodal-AP systems. Beginning with a three-dimensional baseline bimodal-AP particulate propellant (FAP and CAP particles), the system complexity was decreased (in order to better isolate system behavior) to a two-dimensional "bimodal"-AP laminate (FAP particles and CAP slabs) and, finally, to one-dimensional quasi-homogenous monomodal-AP pocket matrix. The use of high-speed video imaging of the burning surface allowed for in-situ observations of aluminum behavior (extent of agglomeration, location of ignition, etc.) without altering the combustion environment.

Figure 1 shows a schematic of the various propellant formulations used in this study. Table 1 gives a summary of the propellant formulations. The baseline formulation (Fig. 1a) was a wide-distribution 70% bimodal-AP, 16% aluminum, 14% HTPB-binder propellant, by mass. In this wide-distribution propellant, the 2-μm FAP loading was near its limit of 44% and the CAP was 26%. The pocket matrix (excluding the CAP, Fig. 1c) mass loadings were 31% Al, 52% FAP, and 17% binder. This gave a FAP/HTPB-binder ratio of 75/25. The latter formulation (matrix only) was used to investigate the behavior of aluminum in the one-dimensional oxy-fuel-matrix premixed flame region, without the influence of CAP/matrix flame contributions. To study these CAP/matrix flame contributions on aluminum behavior in a nearly steady, two-dimensional system, CAP was added in the form of planar slabs (instead of particles) to the outside of the pocket matrix forming a two-dimensional laminate system (Fig. 1b). To investigate the influence of aluminum loading, the mass percentage of aluminum in the fuel layer was reduced from the 31% baseline value to 15% (maintaining the 75/25 AP/binder ratio) in a variation of the baseline formulation. Ingredient Al particle size was also studied by increasing from the baseline 15-μm value to 30 and 95 μm. This systematic approach allowed for the integrated study of aluminum ignition and agglomerate behavior on the surface in relation to the complex AP/HTPB-binder flame structures by selectively including or excluding different parts of the AP/binder flame structure.

The aluminized matrix used for both the monomodal-AP pocket matrix experiments and as the fuel layer in the laminates was created by mixing the uncured HTPB (R45M) prepolymer binder (with DOA, ODI, and Tepanol included) with the curing agent, isophorone diisocyanate (IPDI). The uncured HTPB-binder was preloaded (near the monomodal-AP limit for solids loading) with 76% by mass, 2-μm FAP. With IPDI included the FAP loading was 74.5%. Next, Valimet aluminum powder (H-15), nominally spherical 15-μm, was added and the composite was thoroughly mixed. The aluminized polymer matrix was placed under a vacuum for a minimum of 1 h in order to minimize porosity and remove air bubbles. The matrix was then placed an oven at 338 K for seven days at atmospheric pressure in order to cure the polymer.

The aluminized laminate propellants were manufactured according to the laminate construction method described by Price et al. [1]. First, the outer oxidizer layers were pressed into discs from 200-μm coarse-AP at 170 MPa for a minimum of 30 min. When the degassing stage of the inner fuel layer (the aluminized matrix) was completed, the laminate was constructed by depositing the aluminized matrix between the coarse-AP discs. Fuel-layer thickness was controlled using spacers. The laminates were then cured. Laminates with varying fuel layer compositions (described previously) and thicknesses between 0.05 and 1.25 mm were constructed resulting in total sample thicknesses ranging from about 1 to 3 mm.

A similar procedure was followed to manufacture the wide-distribution, bimodal-AP particulate propellants. Two mixtures were created: the first mixture contained 200-μm CAP whereas the second contained 400-μm CAP. All other components in the two mixtures were equivalent.

Once the curing process was complete, the propellant was cut to size (approximately 3 mm in-depth and 4.5 mm in height). The width, or thickness, of both the matrix and composite samples varied from about 1 to 3 mm. The sides of the matrix parallel to the line of sight of the camera (where the CAP slabs would be if the propellants were in laminate form) were coated with epoxy or petroleum jelly to inhibit

Table 1 Propellant formulations by mass percent

Laminate and particulate propellants	%	Particulate propellants	%	Matrix propellants	%	%
AP	70	FAP	44	FAP	52	64
Binder	14	CAP	26	Binder	17	21
Al	16	Total AP	70	Al	31	15

them from burning. An inhibitor was also placed on the outer surface of the composite propellant samples.

The samples were burned in a windowed combustion chamber. Nitrogen purged the system of combustion products while maintaining the chamber pressure at desired test conditions, typically 3 through 40 atm. Relatively low pressures were desirable for this study because aluminum agglomeration is known to be almost universally more extensive at lower pressures. If one can show reduced aluminum agglomeration at low pressures, that is the more challenging pressure regime. The nitrogen entered the chamber from the bottom and exhausted from the top. An image of the unburned sample was captured prior to ignition. This was to ensure proper sample orientation and as a postexperiment reference such as for fuel layer position in laminate propellants. Combustion was initiated on the top surface of the sample via a CO_2 laser. As soon as ignition of the propellant was observed, laser flux was removed in order to allow self-sustained deflagration in the sample.

Baseline matrix samples were burned in the pressure range from 4 to 21 atm. Because of their composition (fuel-rich with very-FAP) these materials were near a flammability boundary where they may or may not have sustained self-deflagration. They therefore required a few seconds of initial preheating via the laser ($\sim 100\ \mathrm{W/cm^2}$).

A Phantom V7.0 high-speed, CMOS camera was used to capture images for experiments. Spatial dispersions as high as 3 μm per pixel were obtained by using a system of Nikon extension bellows attached to the camera. Images were captured at rates up to 10,000 frames per second with exposure times of 2 μs or longer. Outside lighting was useful on experiments with longer exposure times ($> \sim 80\ \mu$s). A NorthStar 250 W tungsten halogen lamp provided direct illumination, replacing the previous techniques of backlighting and frontal illumination via light reflecting off a mirror. Because of imaging constraints, there was a possibility of aluminum particle size overestimation if the droplets were out of focus or were saturated (and, thus, not able to distinguish between the droplet and the surrounding aluminum oxide smoke).

IV. AP/HTPB Thermochemical Implications and Flame Structure

Much of the behavior of Al in the present baseline wide-distribution AP/HTPB/Al propellant is explainable from AP/HTPB thermochemical equilibrium and flame structure considerations. Mixture fractions of oxidizer and fuel species generated by decomposition of AP and HTPB, respectively, vary spatially (two-dimensional laminate and three-dimensional propellant) and temporally (three-dimensional propellant). Thermochemical equilibrium temperatures for AP and HTPB (holding back Al participation) based on local mixture fractions at various spatial locations in the gas phase region give a useful indication of the flame conditions to which aluminum might be exposed. The reason the laminate system mixture fractions are relatively steady is because it is heterogeneous laterally (perpendicular to the direction of burning) at the length scale of the fuel layer thickness but homogeneous in the streamwise direction (direction of burning). The three-dimensional particulate propellant is also heterogeneous in the direction of burning at the length scale of the CAP, and thus its mixture fractions vary spatially in the streamwise direction at an instant of time or vary temporally at a fixed point in space.

Figure 2 displays the AP/HTPB equilibrium (adiabatic flame) temperature (T_{AFT}) as a function of AP mass percent at a system pressure of 14.8 atm. The maximum (stoichiometric composition) temperature is about 2900 K corresponding to 89% AP. This temperature would apply to CAP/matrix flames in the split-diffusion condition as well as in the partially premixed condition if the flames were close to the merged state (not excessively fuel-lean as with very thin fuel layers). At 75% AP the temperature is about 1800 K; this composition corresponds to the FAP/binder matrix premixed flame without Al participation. At 100% AP the temperature is 1400 K, the theoretical (equilibrium), adiabatic AP monopropellant flame temperature.

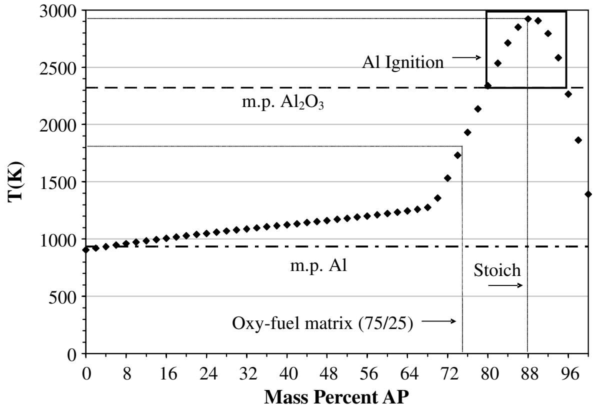


Fig. 2 Theoretical (equilibrium) adiabatic flame temperature of AP/HTPB-binder as a function of mass percent AP at 14.8 atm.

Figure 3 shows a schematic diagram of the AP/HC flame structure for these wide-distribution propellants that has been derived in this [20] and previous studies [6] along with corresponding theoretical temperatures. The diagram in Fig. 3 applies primarily to two-dimensional laminates with excess CAP (overventilated) but the concepts apply to three-dimensional particulate propellants on a local, instantaneous basis. As noted, the fuel-rich 75/25 FAP/HTPB matrix burns in an essentially one-dimensional premixed flame achieving a temperature of approximately 1800 K fairly uniformly laterally within tens to hundreds of micrometers of the matrix surface, depending on pressure. The oxidizer-rich CAP, which theoretically goes to 1400 K, in practice exhibits a monopropellant flame temperature of approximately 1200 K. In both the fuel matrix and CAP regions, away from the CAP/matrix interface, the surface temperature is on the order of 900 K. If mixture conditions can support it, the CAP/matrix diffusion flame would be located near the CAP/matrix interface, where the surface temperature may be higher, particularly at higher pressures, due to the presence of the LEFs.

The key to AP/HC flame structure in wide-distribution propellants is the CAP/matrix interaction flame. CAP/matrix interaction flame conditions are shown in Fig. 3 for two pressures, relatively high and low. (The quantitative meaning of "high" and "low" is discussed next in connection with Fig. 4.) At higher pressures the CAP/matrix flame is in the split-diffusion regime. Dotted lines show the location of theoretical stoichiometric-level surfaces formed by diffusive mixing of the oxidizer and fuel species emanating from the CAP and matrix flame regions. These surfaces can be thought of as virtual diffusion flame surfaces. If diffusion flames form it is along these surfaces at some distance from the propellant surface. Near the propellant surface the partially premixed LEFs form with a fuel-rich branch on

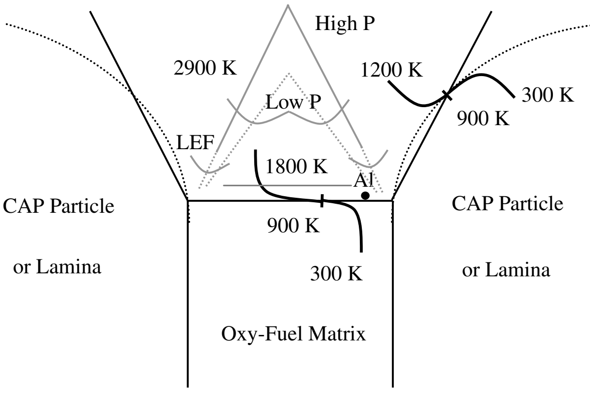


Fig. 3 Schematic diagram of AP/HC flame and near-surface temperature structure showing CAP monopropellant flame (1200 K), FAP/binder-matrix flame (1800 K), and CAP/matrix flame at high pressure (split-diffusion with LEF, 2900 K) and at low pressure (merged, partially premixed, ≤ 2900 K).

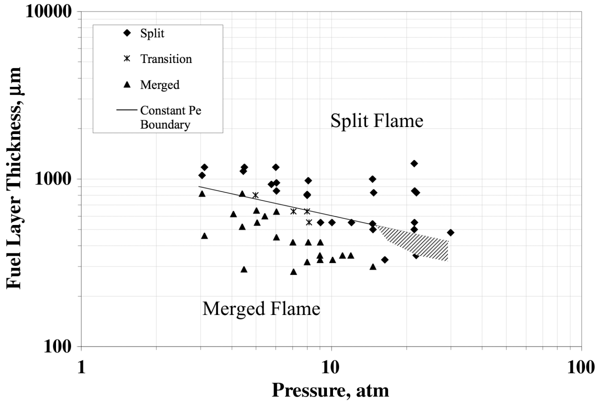


Fig. 4 Flame-regime map for CAP/matrix interaction flame of two-dimensional laminate propellants of 75/25 FAP (2-μm)/HTPB-binder oxygenated fuel matrix (inner layer) with excess CAP lamina (outer layers).

the matrix side and a fuel-lean side on the CAP side. The temperature at the diffusion flames and at the stoichiometric center of the LEFs approaches 2900 K.

Consider now what happens to the CAP/matrix flame structure as pressure decreases: the LEFs move farther from the surface and widen laterally due to slower reaction kinetics relative to diffusive mixing. At the same time the stoichiometric-level surfaces close over the fuel layer closer to the propellant surface; i.e., the diffusion flame height decreases. This is due to the usual reduction in mass flux (burning rate) with decreasing pressure, and corresponding decrease in Pe. (Most sketches of this in the literature [1,2,12,19] incorrectly depict the stoichiometric-level surfaces as staying at the same location as pressure changes and only move the LEFs.) At some point the fuel-rich branches of neighboring LEFs merge; the flame structure transitions to the merged regime. At the condition of merger the flame LEFs still have stoichiometric flame temperature locations reaching 2900 K but as pressure continues to decrease, fuel-lean conditions prevail in the CAP/matrix interaction region, due to excess CAP, and the maximum flame temperature falls below 2900 K.

This transition behavior, which is illustrated in Fig. 3 in terms of constant fuel-thickness and varying pressure, can also be thought of in terms of constant pressure and varying fuel thickness. For a given pressure, beginning at “large” fuel thickness, the CAP/matrix flame regime is split-diffusion. As fuel-thickness (or more generally diffusion length scale, e.g., AP particle size) decreases, the CAP/matrix flame transitions to the merged, partially premixed regime. Dimensional values of pressure and length scale of the CAP/matrix interaction flame regime have been mapped for the present baseline system of overventilated (excess CAP) 75/25 FAP/matrix laminate, and are shown in Fig. 4. The data points are the results of individual tests; the solid line is the inferred boundary between the split- and merged flame regimes. (Sparsity of usable test data above 15 atm results in definition of only a broader transition region.) As seen in Fig. 4 the split flame regime occurs at high pressures and/or fuel thicknesses. As pressure and/or fuel-thickness decrease the separate diffusion flames merge. The boundary between split and merged regimes, which must of necessity be defined somewhat arbitrarily, is taken here similar to the previous nonaluminized study [6] (approximately 35% apparent protrusion at the center of the fuel layer). The transition boundary can be described theoretically in terms of a constant Pe condition, according to conserved-scalar (mixing fraction) theory [20,21], with a theoretical boundary slope of $-n$, the burning rate pressure exponent, as discussed elsewhere [20].

Aluminum behavior can be related to the preceding conditions as follows. Aluminum melts at approximately 930 K, close to the surface temperature. Thus some melting of Al on the matrix burning surface can be anticipated. The aluminum oxide shell melts at about 2320 K. Al ignition generally does not occur until this temperature is reached and the protective oxide shell melts. According to Fig. 2, there is a “window” region of AP/HTPB-binder mixture ratios that have adiabatic flame temperatures greater than 2300 K. It is within this window region, where local gas mixture composition is between slightly less to slightly greater than the stoichiometric mixture, that ignition of Al can be expected. Thus, aluminum ignition can occur in regions where a CAP/matrix diffusion flame or sufficiently near-stoichiometric premixed flame is present.

V. Aluminum Behavior Results and Discussion

A. Pocket Matrix Propellant (One-Dimensional Steady Flame)

To help characterize the behavior of the aluminized propellant within the pocket region, excluding the influence of the coarse AP, experiments are conducted on the fuel matrix alone. These pocket matrix propellants are fuel-rich and contain monomodal FAP. Experiments performed at the low end of the examined pressure range burn completely, whereas those in the intermediate pressure region mostly burn, but occasionally quench. Tests at the upper end of the pressure range tend to quench or do not burn without laser assistance (preheating).

Extension of the nonaluminized matrix work conducted by Freeman et al. [22,23] to an AP/binder ratio of 75/25 indicates that 2-μm AP matrix samples should burn, at least within a narrow pressure range around 20 atm. This was not observed to be the case by testing nonaluminized pocket matrix samples. This difference or apparent minor discrepancy is not significant since this fuel-rich system is near a combustion stability boundary and can easily go either way depending on small systematic or stochastic variations. The aluminized matrix, however, did burn at least partially over most of the pressure range. From this it can be concluded that the presence of aluminum in the 75/25 FAP/binder matrix aids in the combustion of the matrix at low pressures even though most of the aluminum particles do not ignite at the surface. It is postulated that the increased thermal conductivity of the matrix (due to the presence of aluminum) provides enough additional in-depth, conductive heating of the solid propellant for these low-pressure samples to burn whereas the nonaluminized matrix samples do not. The thermal conductivity of aluminum is two to 3 orders of magnitude greater than both AP and HTPB. For example, adding 18% Al to an 86/14 AP/HTPB propellant increases the thermal conductivity by 20% [24]. For the formulations studied in the present work, considering the pocket concentration of aluminum is even higher at 31%, by mass, it is justifiable to expect the thermal conductivity of the aluminized matrix to be more than 20% higher than a nonaluminized matrix.

The most interesting finding regarding aluminum behavior in the 75/25 FAP/matrix has to do not with the (slightly stabilizing) effect of aluminum on the FAP/matrix combustion but with the effect of FAP/matrix combustion on aluminum accumulation/agglomeration behavior at the surface. Figure 5 shows an image of the baseline aluminized fuel matrix burning at 4.4 atm. Low lighting makes distinguishing features from a single frame difficult. Therefore lines are hand-drawn to designate features such as individual parent Al particles on the surface, accumulated Al on the surface, and accumulates in the gas phase being dragged away from the surface.

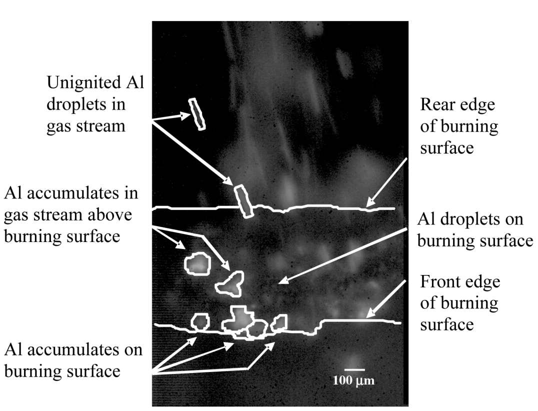


Fig. 5 High-speed camera image of one-dimensional baseline (75/25 FAP/HTPB) fuel matrix (nonlaminate) burning at 4.4 atm.

(Identification of these features is much easier from movies.) In all matrix burning or quenching cases, only some of the aluminum particles ignite near or on the surface with the rest leaving the image frame unignited (Fig. 5). This is consistent with thermochemical equilibrium considerations as noted, which show that the pocket matrix flame can not achieve sufficient temperature to melt the aluminum oxide shell and ignite Al on the surface. Small clumps or accumulates of aluminum particles, however, are seen both on and off the surface (Fig. 5). The size of these accumulates is approximately 100 μm but if melted and agglomerated they would form agglomerates of only about 40 μm. What is significant here and a major unique finding of this work is that Al leaves the matrix surface largely unagglomerated. Previous studies of more conventional formulations [9,10,12] have looked at larger FAP and/or lower FAP/binder ratios and have typically seen much more extensive surface Al agglomeration. In this unique mixture of FAP at the 75/25 loading level, even though the oxide melting temperature is not achieved, there is still not extensive agglomeration. It is postulated that the reason this mixture is able to reduce agglomeration so much has to do with higher normal gas velocities close to the burning surface that exert aerodynamic drag on the Al particles and are able to lift them away from the surface.

B. Laminate Propellant (Two-Dimensional Steady Flame)

To simulate CAP/matrix interaction flames in a two-dimensional, steady fashion, laminates of pressed AP are added to the outside of a layer of pocket matrix. As noted, the outer CAP/matrix flame structure of burning laminates typically exhibits one of two flame types: split (diffusion) or merged (partially premixed). Previous experiments on AP/HTPB flame structure without aluminum used UV and/or IR imaging to distinguish a gaseous flame using HCl or OH* [6]. The broadband visible imaging approach used in this work can not see excited gaseous molecules directly. Because of the inclusion of aluminum, however, a different method of delineating AP/HTPB flame structure can be used. Aluminum ignition is associated with the appearance of a luminous burning droplet as well as smoke in the burning laminates; thus smoke traces emanating near the surface of the fuel layer are used to define the flame as split (diffusion flame) or merged (partially premixed flame). See also [20] for a detailed discussion of the flame structure characteristics of these propellants.

Figures 6 and 7 are baseline laminates that show gas phase and surface characteristics of a split flame and a merged flame, respectively. The outer CAP slabs are lighter in color than the fuel layer, and a clearly defined outer-AP/fuel matrix interface is visible. The fuel layer is flat for both flame types. Aluminum droplets cover the surface and are present in the gas stream above the laminate fuel layer. Bright spots of combusting aluminum and their smoke trails are visible in the gas stream above the surface. The origins of these smoke traces and burning aluminum indicate the locations of ignition of the aluminum droplets. In the split flame regime (Fig. 6) Al ignition occurs at the overventilated diffusion flame "tent" or canopy (inverted-V shape; see Fig. 3, "High P") above the surface. In the merged flame regime (Fig. 7) the merged, partially premixed CAP/matrix interaction flame can be inferred by the smoke traces emanating from across the entire burning surface and not just near the laminate interfaces (Fig. 3, "Low P"). This outer-canopy partially premixed flame sits farther away from the surface than the inner premixed flame layer created by the premixed FAP/matrix (Fig. 3).

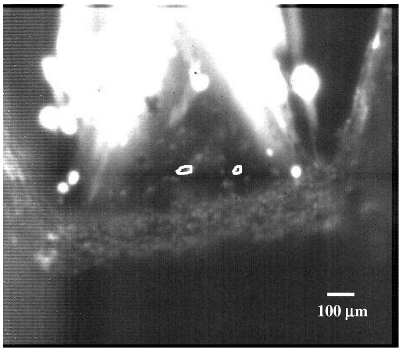


Fig. 6 Baseline laminate propellant (75/25 FAP/HTPB matrix with CAP slabs) with fuel layer thickness of 1000 μm burning at 14.6 atm. CAP/matrix interaction flame is in split (diffusion) flame regime (see Fig. 3, "High P"). Al accumulates are highlighted.

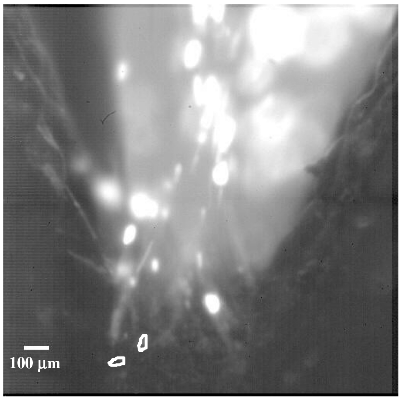


Fig. 7 Baseline laminate propellant (75/25 FAP/HTPB matrix with CAP slabs) with fuel layer thickness of 550 μm burning at 5 atm. CAP/matrix interaction flame is in merged (partially premixed) flame regime (see Fig. 3, "Low P"). Al accumulates are highlighted.

In all baseline and the 15% Al variation from baseline laminate propellants examined, the majority of the aluminum remains unagglomerated (diameters ranging from about 20–40 μm) when it leaves the surface. This is consistent with the nonagglomerating behavior seen in matrix-only (one-dimensional) baseline propellants. However, in the laminates, unlike the matrix-only propellants, the Al leaving the fuel surface eventually ignites. This is because the additional oxidizer from the CAP slabs allows the system to support either canopy diffusion flames or near-stoichiometric (outer-canopy) partially premixed flames where the mixture-fraction ratio is in the window region of Fig. 2. It is also observed that the limited amount of accumulation of Al that does occur on the fuel matrix surface in laminates is less than in nonlaminates. This may be related to the increased burning rate of the laminate propellants as compared with the matrix-only samples and higher gas velocities near the burning surface.

Also occasionally seen in the (baseline and 15% Al variation) laminate propellants, are unignited accumulates leaving the surface and entering the flow field as small chains (Fig. 8). The aluminum particles "stick" together as described by Price [9] but do not coalesce into large agglomerates, possibly, until farther downstream (near the stoichiometric flame) where temperatures are more favorable for oxide layer melting at the onset of ignition (see window region highlighted in Fig. 2).

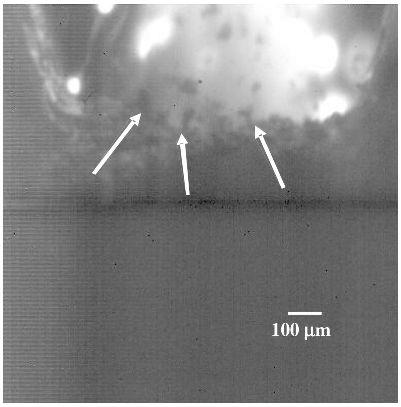
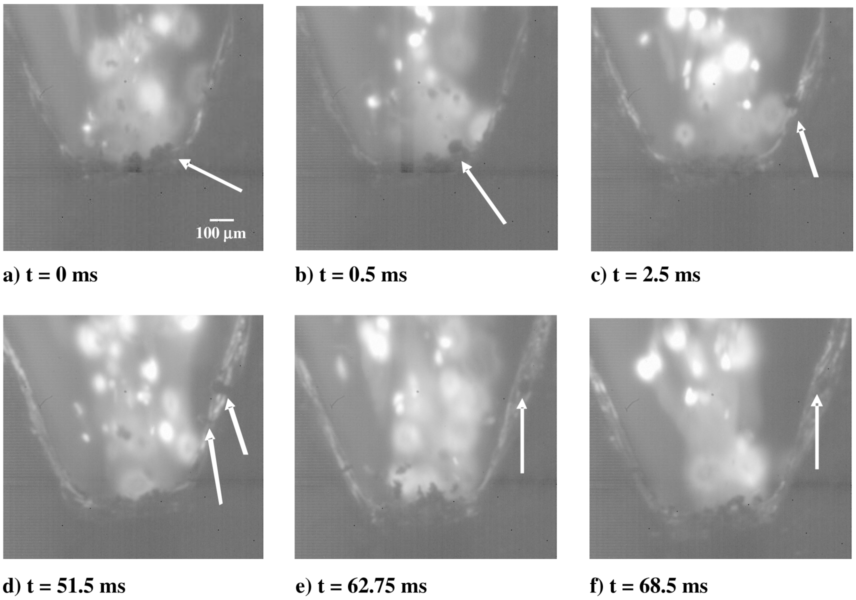


Fig. 8 Chains or filigrees of aluminum particles on the surface of a baseline laminate at 8 atm with a fuel layer thickness of 800 μm. Al accumulates are highlighted.



a) t = 0 ms b) t = 0.5 ms c) t = 2.5 ms

d) t = 51.5 ms e) t = 62.75 ms f) t = 68.5 ms

Fig. 9 A series of images showing a droplet of aluminum moving up the CAP slab and then flattening out onto the surface of the CAP. This baseline laminate has a fuel layer thickness of 350 μm and is burning at 12 atm.

The baseline laminate propellant movies also indicate that Al can and does migrate laterally across the burning surface, generally from fuel matrix to CAP. A close look at laminate propellant movies reveals aluminum particles "rolling" up the CAP lamina. In Fig. 9 of a baseline laminate with a 350-μm fuel layer at 12 atm, an aluminum droplet "rolls" up and flattens out on the face of the CAP slab. Initially, (a), a few particles of aluminum are seen on the fuel layer just to the side of the CAP/fuel layer interface. These separate particles form a single droplet of aluminum (about 56 μm) seen in frame (c). Over the course of the next 50+ ms, the aluminum droplet moves up the surface of the CAP slab. During this time, and shown in frame (f), a small chain of aluminum particles moves up the CAP slab just below the droplet. Frames (e) and (f) show the aluminum droplet flattening out onto the surface of the CAP. The dark spot, approximately 66 μm wide, indicates the location of the aluminum droplet on the slab. It is larger than the original particle diameter suggesting that the aluminum droplet has flattened or otherwise spread out onto the CAP surface. The mechanism of lateral aluminum migration on the surface is not well understood. There are possibly tangential fluid velocities at the surface in the gas, liquid, or both. However, the relative strength of their associated drag forces on Al particles is not well understood. Nevertheless, the mechanism is an important one as it is seen again in bimodal-AP (three-dimensional particulate) propellants to even a greater extent and is mentioned next.

C. Bimodal Particulate Propellant (Three-Dimensional Unsteady Flames)

Aluminum behavior in particulate (three-dimensional) bimodal-AP propellant is also investigated. Wide-distribution, bimodal-AP propellants are created by intermixing CAP particles (200 or 400 μm) with the matrix. High-speed imaging of the burning surface of aluminized heterogeneous composite propellants show that the system exhibits similar mechanisms to those observed in laminate propellants but also reveals some characteristics unique to the three-dimensional geometry of particulate propellants with CAP particles.

Figure 10 shows the burning surface of 400-μm CAP propellant at a pressure of 3 atm. Parent aluminum particles can be seen on the surface of the fuel matrix between CAP, similar to the fuel matrix in laminates and the fuel matrix alone. Aluminum particles also cover the surface of the CAP particles that are partially imbedded in the propellant surface. Ignited aluminum burns in the gas above the propellant as indicated by the white streaks. In the movies, some of the aluminum particles can be seen crossing portions of the surface of the propellant and gathering on or near the CAP particles, as discussed next.

The collection of aluminum on the surface of CAP particles leading to aluminum agglomerate formation is a new characteristic of particulate-composite propellants not observed in laminates. As the propellant surface burns down, aluminum particles settle onto freshly exposed CAP particles. Additional aluminum gathers on CAP particles via the surface migration mechanism described in the previous section. As a CAP particle burns away, a relatively "flat" accumulation of aluminum particles remains, which balls up and typically ignites as a single, large agglomerate but, occasionally, as multiple smaller agglomerates. The diameter of this large agglomerate is smaller than the footprint of the AP particle on or near which it accumulated. Figure 11 gives a sequence of images from a movie showing this process. Here, a nonspherical CAP particle

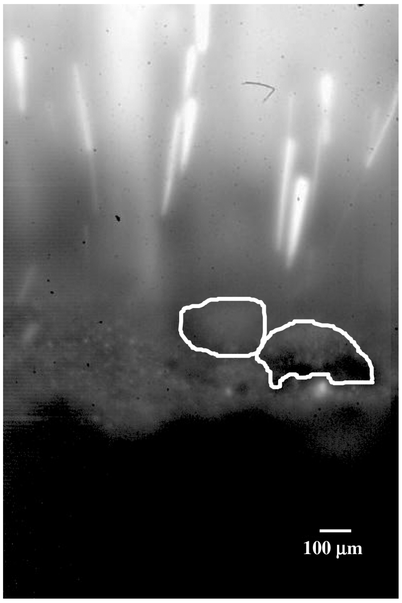
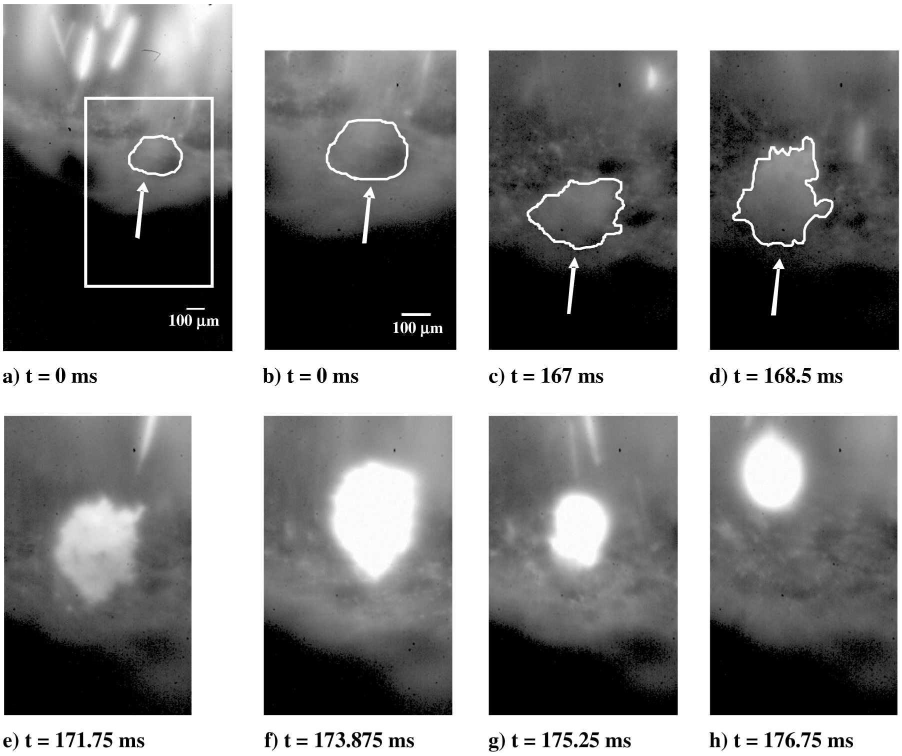


Fig. 10 Image of a 400-μm CAP baseline particulate propellant burning at 3 atm. CAP particles, hand-drawn outline in white, can be seen imbedded in the surface of the propellant and covered in aluminum particles. The white streaks in the top half of the image are burning aluminum.



a) t = 0 ms b) t = 0 ms c) t = 167 ms d) t = 168.5 ms

e) t = 171.75 ms f) t = 173.875 ms g) t = 175.25 ms h) t = 176.75 ms

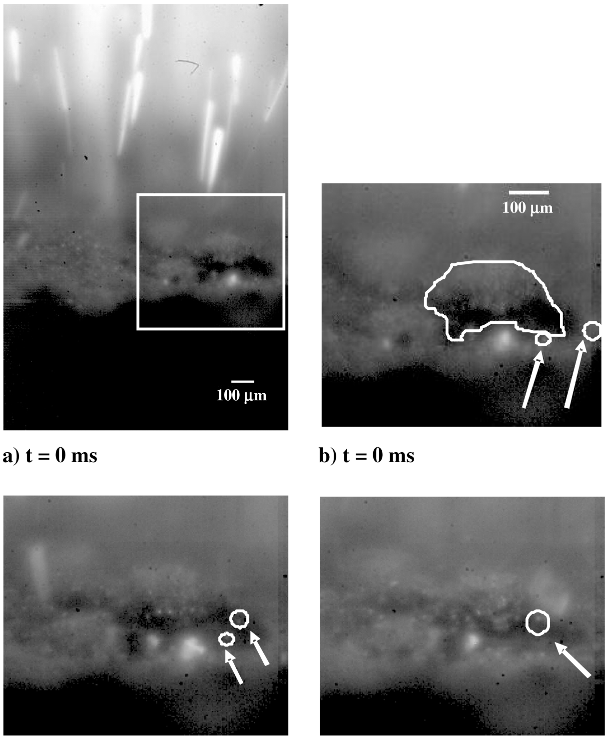
Fig. 11 CAP particle [approximate size in (a) 260 μm wide] shown covered with aluminum particles that accumulate on its surface as the propellant burns. Outlines hand-drawn in white to make the particles easier to identify. Diameter of burning agglomerate in (h) is 200 μm. This is a 400-μm CAP baseline propellant burning at 3 atm.

(approximate width of 262 μm) sits imbedded in the propellant (a, b). Aluminum particles gather on its outer surface and retain a "dome" shape as the CAP burns underneath and as the propellant burns down around it. Once the CAP particle has burned away, the remaining aluminum aggregate, now appearing more flat than "domed," begins to rise up on its side (c). The top part of the aggregate is far enough from the surface to encounter the higher temperatures of the outer CAP/matrix flame regime, and a thermal wave propagates back down into the aggregate (d). The aggregate separates from the surface (e) and ignites (f) as it begins to coalesce (g) into an agglomerated sphere (h). The diameter of this agglomerate droplet is 204 μm, which is smaller than the size of the original CAP particle on which it formed.

The phenomenon of lateral migration of Al on the surface is also seen in three-dimensional particulate propellants as it was seen in two-dimensional laminates. Parent aluminum is observed to migrate on the surface to the locations of CAP particles where it then accumulates. Figure 12 shows this process in a 400-μm CAP propellant mixture at 3 atm. As seen in Fig. 12, a CAP particle, covered in aluminum particles that form a dome shape, sits imbedded in the propellant surface (a, b). Aluminum particles, with diameters of about 30 μm or smaller, migrate on the propellant surface to the CAP particle surface where they climb the dome (b–d) and accrue. This takes place during a 1.5 ms time interval.

Aluminum migration in the particulate propellants is comparable to the aluminum rolling up the surface of the CAP slabs in laminate propellants. This migration behavior is not as prevalent in the two-dimensional geometry as it is in the three-dimensional geometry. Lateral migration on two-dimensional AP laminates may be more difficult to see optically. There is a better camera angle on the heterogeneous composite propellants where the front and top of the CAP can be seen as opposed to the side profile angle of the laminate propellants. Likewise, the steeper climb the aluminum particles have to make up the CAP slabs in the laminates might inhibit the behavior somewhat. What appears like a relatively unimportant (infrequent) process in two-dimensional is shown to be more frequent and prevalent in three-dimensional.

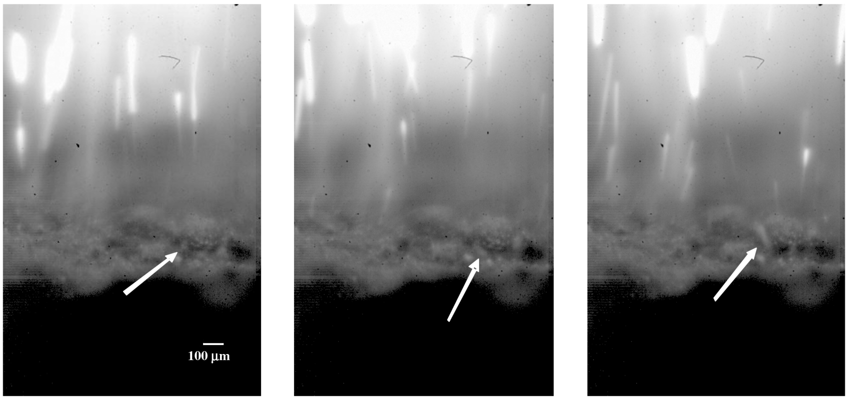
Regarding the behavior of Al in the matrix pocket that does not migrate to CAP particles, it is similar to that seen in laminates: there is a unique tendency for reduced aluminum agglomeration with ignition of aluminum occurring above the surface. Because of the three-dimensional unsteady nature of the particulate propellants, it is not nearly as easy as it is in two-dimensional laminates to identify the



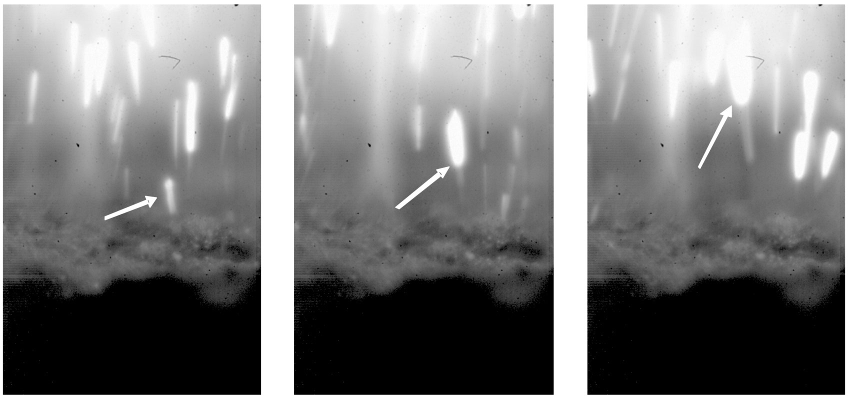
a) t = 0 ms b) t = 0 ms

c) t = 0.5 ms d) t = 1.25 ms

Fig. 12 Aluminum particles migrating on the propellant surface and up the sides of CAP particles in 400-μm CAP baseline particulate propellant formulation burning at 3 atm. Outlines are hand-drawn in white to make the particles easier to identify.



a) t = 0 ms b) t = 0.125 ms c) t = 0.25 ms



d) t = 0.375 ms e) t = 0.5 ms f) t = 0.625 ms

Fig. 13 Baseline 400-μm CAP particulate propellant, burning at 3 atm: aluminum particles seen leaving the surface unagglomerated and igniting downstream. For the 30-μm particle highlighted, the bright luminosity of ignition can be seen at the tip of the aluminum streak in (d).

outer CAP/fuel matrix flames that ignite Al leaving the fuel matrix portion of the surface. The spatial location of Al ignition is so random in three-dimensional that identifying it as occurring at, for example, a CAP/fuel matrix canopy diffusion flame, would be difficult. In this regard two-dimensional laminates give important and unique insight.

As in laminate propellants, the majority of aluminum ignition occurs above the surface in outer-canopy CAP/fuel matrix flames where temperatures are high enough to melt the aluminum oxide shell. This can be seen in Fig. 13 for a particular droplet designated by the arrow; the particle leaves the surface and ignites at the end of frame (d) where the bright tip indicates the onset of ignition.

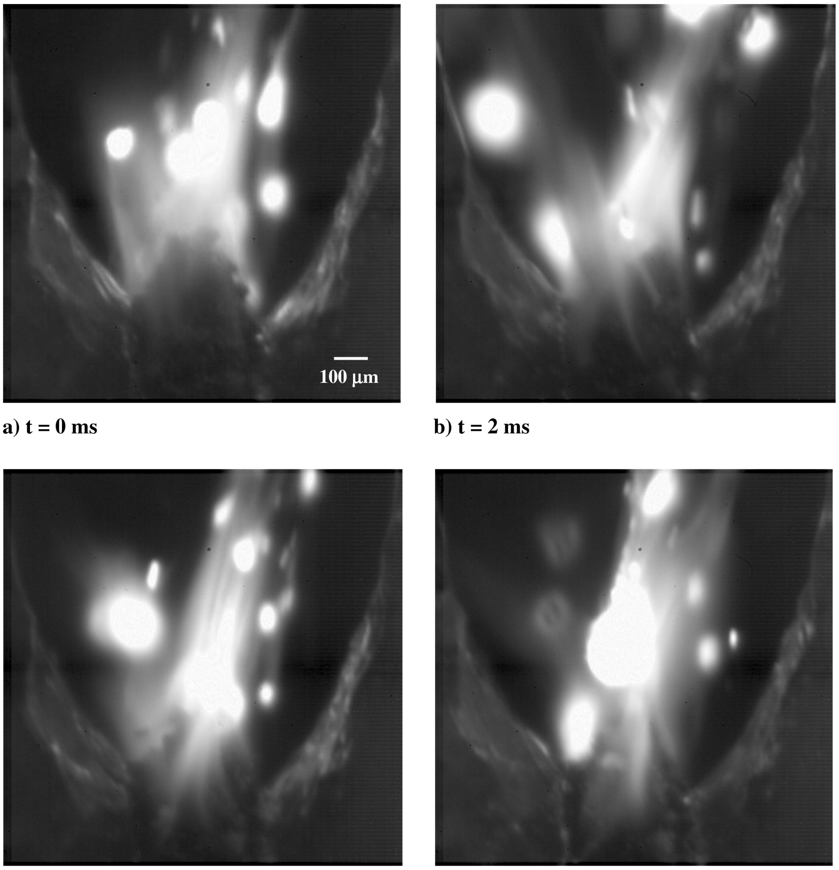
Regarding the overall agglomeration behavior of this unique formulation of wide-distribution FAP/CAP propellants, the following observations can be made. Highly FAP-loaded fuel matrix is unique in reducing Al agglomeration as compared with conventional (e.g., lower FAP loading or larger FAP-size) propellant formulations. The presence of CAP particles does allow for Al agglomeration but the number of these agglomerates is reduced compared with conventional (lower FAP/CAP-ratio) propellants because of the reduced number of CAP particles. The majority of the aluminum leaving the surface of the bimodal composite propellant remains unagglomerated, as illustrated in Fig. 13. In Fig. 13, the average diameters of the aluminum droplets are about 30 μm and are similar in scale to that observed in laminate propellants. This reduced agglomerate rate and size is in contrast to the pocket model [7,8], which suggests that a bimodal composite propellant like those in the present work should produce agglomerates the size of the CAP.

D. Variations from Baseline Formulation

Several formulation variables were changed to test their influence on aluminum behavior, including FAP/binder ratio, Al loading, and Al ingredient particle size. Figure 14 shows images of a laminate with a reduced FAP/binder ratio, 58/42 instead of 75/25, burning at 18 atm with fuel-thickness of 300 μm. The 58/42 matrix is so much more fuel-rich than the 75/25 matrix that it is not even close to being able to burn on its own and requires heat from the CAP/matrix interaction flame. As a result, when the pressure-thickness conditions are such that the CAP/matrix flames are in the split, diffusion flame mode, as they are in Fig. 14, the matrix surface burns on a slant, protruding into the gas phase. More importantly, because of the reduced matrix flame temperature, the gas-velocity conditions near the matrix surface are apparently not as favorable for dragging Al off the surface, as much more extensive agglomeration of Al is seen for the 58/42 matrix. The extent of agglomeration in the 58/42 matrix is more representative of conventional propellants, where typically thousands of parent ingredient Al particles combine to form a single agglomerate, whereas for 75/25 matrix the number is on the order of only ten to 30. If the FAP/binder ratio was kept at 75/25 and Al loading reduced from 31 to 15%, the extent of agglomeration stayed low, i.e., at about ten to 30 ingredient particles combining. These small agglomerates still left the matrix surface unignited and did not ignite until they encountered the hot, CAP/matrix flame. Overall the behavior of Al and the matrix stayed about the same at 15% Al as at 31%.

Variations in size of ingredient Al (increases from 15 μm to 30 and 95 μm) were also tried, in both laminates and particulate propellants. Figure 15 shows a laminate with 30-μm Al. As seen in Fig. 15 aluminum leaves the surface unignited and ignites as soon as it reaches the CAP/matrix diffusion flame. The aluminum does not agglomerate much but does form small chains or filigrees. There is some lateral migration of aluminum, mostly in the region near the AP/fuel layer interface. This movement, however, is not as prevalent as it is in baseline (15-μm Al) laminates. For the most part the behavior of Al, matrix combustion, and CAP/matrix flame was the same with 30-μm Al as with 15-μm Al, with the exception of slightly reduced lateral migration of Al on the surface.

Figure 16 shows a particulate propellant with 95-μm Al (200-μm CAP) and otherwise baseline conditions. With this large of Al, there



a) t = 0 ms
b) t = 2 ms
c) t = 4 ms
d) t = 5.8 ms

Fig. 14 Effect of reduced FAP/binder ratio: 58/42 FAP/HTPB-binder laminate with a 300-μm fuel layer burning at 18 atm. The extent of Al agglomeration increases dramatically compared with 75/25 matrix.

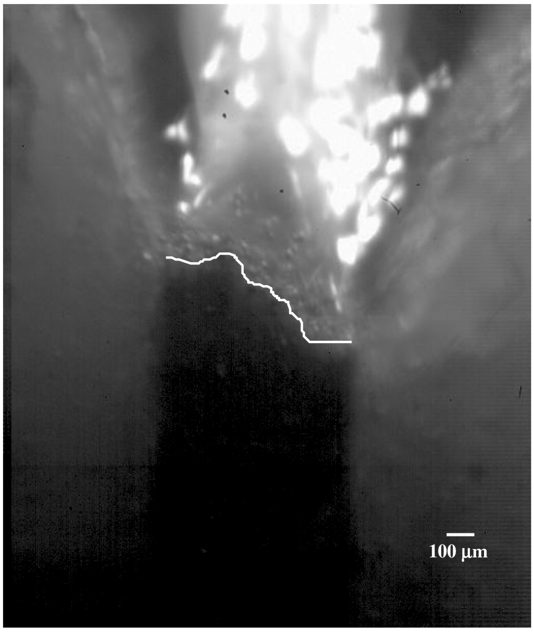


Fig. 15 Effect of larger ingredient Al size: 30-μm Al (31%) in 75/25-matrix laminate propellant with a fuel layer thickness of 900 μm burning at 21.4 atm. The surface is hand-drawn in white. Aluminum agglomerates are larger than with 15-μm Al just because of the larger ingredient size, but the degree of agglomeration is still kept relatively low by the favorable FAP/binder flame conditions.

is very little, if any, observable Al lateral movement like that documented in the particulate propellants with 15-μm parent Al. The lack of lateral movement is probably due to the reduced mobility (greater lateral drag forces and inertia) associated with the larger size of the Al particles. They are also much larger than the thickness of the

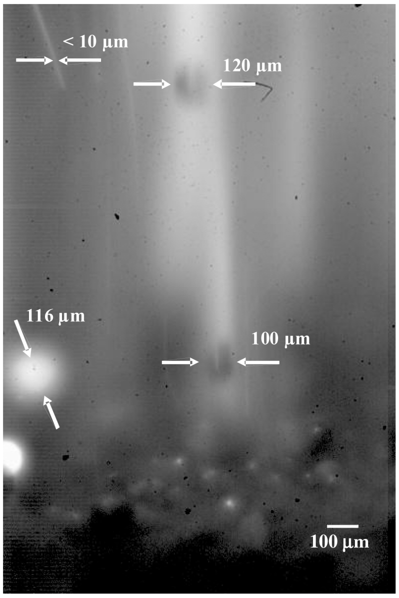


Fig. 16 Effect of larger ingredient Al particle size: 95-μm Al (31%) in particulate propellant (200-μm CAP) with 75/25 matrix burning at 3 atm. The diameters of several features are shown. In spite of larger parent Al particles, the degree of Al agglomeration is still kept relatively low by favorable FAP/binder flame conditions.

binder melt layer and perhaps stuck in the solid phase of the binder (below the melt layer) and retained there until released. Ignition of the Al sometimes occurs on the surface, but mostly it occurs above the surface. Although the CAP particles are not as readily visible as they are in the baseline formulations, the ignition that occurs on the surface is most probably taking place near CAP (near LEFs) where temperatures are higher. Al particles are seen to leave the surface both as individual particles/agglomerates or as a small chain of two or more parent particles, similar to baseline propellant behavior. As expected with larger parent aluminum size, agglomerates are larger than with 15-μm Al, in the 100–160 μm range and tend toward the lower end of that range (Fig. 16). This means only a few parent particles are agglomerating together; however, the physical process of aluminum particles agglomerating together is not observed. It is possible that the apparent agglomerates are not really two or more parent aluminum particles that have joined together, but are simply variations in the original parent ingredient size. Valimet H-95, although nominally called 95 μm, has a mean (50%) size of 120 μm and a broad size distribution (at 10%: 73 μm and 90%: 190 μm). Therefore, the "agglomerates" might be parent ingredient aluminum at the large end of the size distribution. The important point is that for this size of Al (95 μm) it becomes apparent that the extent of agglomeration in terms of the number of particles that combine, is reduced compared with the baseline (15-μm Al) case (the size of the agglomerates is not necessarily reduced though, because of the larger parent particle size).

VI. Conclusions

Al behavior in wide-distribution, bimodal-AP composite propellants with high FAP particle loading and very small (2-μm) FAP is studied with high-speed video imaging. Both agglomerate formation and ignition of Al are explained in terms of and correlated with AP/binder flame structure and conditions. A key finding is low overall agglomeration behavior, even at relatively low pressures (1–30 atm). Agglomerate formation is seen to occur both on the surface of the pocket matrix and on CAP particles. On the pocket matrix agglomeration is minimal, whereas on CAP particles larger agglomerates are formed. The key to the reduction in pocket-matrix agglomeration is thought to be more favorable gas-temperature/velocity conditions associated with the closer-to-stoichiometric (inner) premixed FAP/binder flame at the fuel matrix surface than with conventional (lower FAP loading) matrix pocket formulations. The larger agglomerates formed on CAP particles are fed aluminum by two mechanisms: lateral surface migration from matrix to CAP and settling from above in the direction of burning. Even with the more extensive agglomeration on CAP than on the matrix, the higher FAP/CAP ratio means fewer CAP particles than conventional FAP/CAP-ratio propellants and, thus, fewer large agglomerates formed. Results are confirmed by three sample types: one-dimensional pocket matrix, two-dimensional laminates, and three-dimensional bimodal-AP particulate propellants. Laminates show unambiguously that ignition of Al occurs in the near-stoichiometric outer-canopy CAP/oxy-fuel-matrix flame, whose structure is either split (diffusion) or merged (partially premixed) depending on fuel matrix thickness and pressure, consistent with earlier findings on nonaluminized laminates.

Acknowledgments

Support for this work from the U.S. Department of Energy (UIUC-ASCI Center for Simulation of Advanced Rockets) through the University of California (subcontract number B341494) and the Hermia G. Soo Professorship are gratefully acknowledged. Many thanks to Russell Fitzgerald for his contributions in the area of nonaluminized, oxygenated laminate propellants.

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