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Effect of Multidimensional Flamelets in Composite Propellant Combustion

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Studies of edge burning of oxidizer-fuel laminae were extended by inclusion of different sizes of fine ammonium perchlorate (AP) into the binder lamina to study the combustion zone microstructure in composite-propellant combustion. Different modes of burning in heterogeneous systems resulting from pressure effects, AP particle-size effects, lamina thickness, and AP/binder mix ratios were determined. Results are interpreted in terms of the effects on flame structure and multidimensional processes in the combustion zone.

Introduction

THE detailed processes of composite-propellant combustion are complicated by the microscopic scale of the combustion zone, the hostility of the high-temperature and high-pressure environment, and the microscopically complex and chaotic structure of the propellants. The complexities imposed by combustion microstructure can be reduced or alleviated by the use of laminate propellants, in which the microgeometry and combustion zone are two dimensional. Edge burning of sandwiches, consisting of two laminae of ammonium perchlorate (AP) oxidizer with a layer of polymeric binder in between, has been studied extensively to understand combustion processes of composite propellants.[1–6] Studies have been made of the effect of inclusion of ballistic modifiers in the binder lamina,[3,4] and the effect of different binders.[4] The present study consists of a detailed examination of the effect of the inclusion of granular AP in the binder lamina to make what is referred to as AP-filled sandwiches.

Figure 1 is a sketch showing the principal features of the combustion zone, in which the oxidizer-fuel flames consist of a leading-edge flame (LEF) that stands in the mixing region of the oxidizer and fuel vapors, and a diffusion flame that trails from the LEF up to a point where the fuel vapor is all consumed. The LEF is a region of very high heat release as compared to the rest of the diffusion flame, and contributes most of the heat transfer back to the propellant surface.[7] Considerable insight has been acquired regarding the nature and role of LEFs from the earlier sandwich burning experiments.[1–7] This flame complex of AP-binder-AP sandwiches is also applicable to propellant burning, and the most conspicuous differences between the composite propellants and the sandwiches are the following features: in the propellants—typically fuel-rich—the stoichiometric tip closes over the oxidizer particles, and the stoichiometric tip height is related primarily to oxidizer particle size. The role of the LEF is similar to that with sandwiches except that the flame closure is linked to the oxidizer dimensions (i.e., AP particle sizes) instead of binder lamina thickness, and the nature of the flame complex on each AP particle would differ depending on the size of AP exposed surface and the width of the adjoining binder.

Referring to the flame complex in Fig. 1, the questions addressed here are, how is the flame complex changed by the presence of oxidizer particles in the binder, what is the resulting effect on sample burning rate, and what do the results suggest about the burning of a propellant with multimodal oxidizer size distribution? In a qualitative way, the vapors from very fine AP particles in the binder might diffuse into the binder vapors so quickly that normal self-deflagration would not occur on the particle. If there are many fine AP particles, the lamina may then burn on its own with premixed flame, with a burning rate that may, or may not exceed that of AP laminae. If the particles are large enough, they may burn as individual particles, with normal AP self-deflagration and a surrounding diffusion flame analogous to the one in Fig. 1. If there are enough of these AP particles in the binder, the lamina may burn on its own, with a myriad of flames like the ones in Fig. 2. When particles are near enough to each

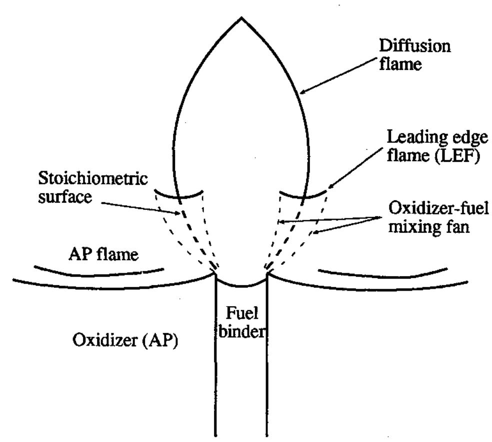

Fig. 1 Flame complex for an AP-binder-AP sandwich.

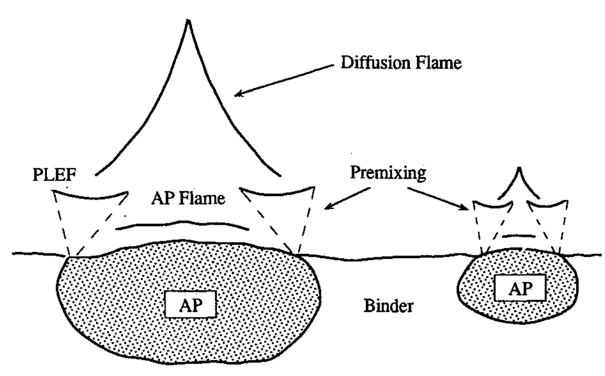

Fig. 2 Flames over AP particles in the matrix.

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other or to the AP lamina, interactive behavior will occur, both through multidimensional heat flow in the condensed phase, and heat and species diffusion in the gas phase.

The AP-filled sandwich samples—laminates of AP-filled binder between two AP laminae—were prepared to investigate these features, using combustion photography, burning rate measurement, and microscopic study of quenched samples. The effects of binder thickness, pressure, percentage of the AP in the binder lamina, and particle size of the AP in the binder lamina were measured and interpreted in terms of qualitative theory of LEF behavior and thermal coupling with the heterogeneous surface.

Experimental Methods

Experimental methods in the present work are mostly routine and detailed elsewhere.[1-5] The principal difference is the inclusion of particulate AP in the binder, by simply hand mixing the mixture before making the sandwich. Sandwiches were made by bonding two AP laminae together with the AP-filled binder. Thickness of the AP-filled binder lamina (matrix lamina) was controlled with spacer shims. The AP laminae was prepared by compacting polycrystalline AP into disks and cutting to shape. The AP was propellant-grade 99.7% purity, low-alkali Kerr-McGee AP size graded at 200 μm. The polycrystalline AP disks were prepared by weighing approximately 1.73 g of ground AP, and pressing at 220 MPa for 2 hr. For the matrix lamina, a nominal size of 10 μm (the 10-μm AP was supplied by K. Kraeutle of the U.S. Naval Weapon Center, China Lake, California) was chosen as the fine matrix-oxidizer, and 33.5 μm was chosen as the coarse matrix-oxidizer. The 33.5 μm was a nominal designation for a screening fraction of ground 200-μm material that passed a 37-μm sieve and was retained in a 30-μm sieve. The polybutadiene acrylonitrile acrylic acid (PBAN) binder was prepared by mixing PBAN prepolymer with epoxy curing agent (Epon 828) and its plasticizer (DOA) in proportions 64.14, 20.86, and 15%.

The amounts and particle size of AP used in the matrix laminae have a significant effect on the rheological properties of the sandwiches. Fractions higher than 70% of AP in the mixture make mixing and handling during sandwich fabrication too difficult. In the present study, the ratios of ingredients were chosen to ensure that the matrix surface area would be fuel-rich (thus ensuring the flamelet closure over the AP particles and fuel-rich conditions above the stoichiometric tips of AP particles in the matrix). The mass-mixture ratios of AP and PBAN binder were chosen as 5:5 and 7:3 (a few samples were made with 8:2 mixtures). Matrix thicknesses were chosen between 125–600 μm, the lower limit being determined by difficulty in sandwich fabrication, and the upper limit by the expectation of no useful results for greater thickness.

Several test samples were cast from the excess matrix mixture for measurement of the matrix burning rate. These propellant-type of samples (matrix samples) were prepared using the same matrix mixtures used in the sandwiches. After the mixture was vacuumed, it was then transferred to rectangular molds of dimensions 20.7 × 11.2 × 2.3 mm, and hand pressed by tapping the mixture with a 1-cm-diam cylindrical Teflon® rod.

All samples (sandwich and matrix) were cured in an oven at 72°C for 7 days. After curing, the matrix samples were cut into rectangular shapes (11.2 × 5.5 × 2.3 mm) and the sandwich samples were sanded down on the edge to form a parallelepiped of the desired dimensions (10 × 7 × 3.0 mm) for burning-rate tests. Equivalent sandwiches without AP in the binder were also made to compare with previously obtained results,[3] and to address the resulting effects of AP particles in the binder.

The principal experimental facilities used here are comprised of a nitrogen-flushed high-pressure combustion chamber with quartz windows for combustion photography, a nitrogen-flushed high-pressure chamber with a burst disk for quenched burning, a video camera-monitor-recorder system, an optical microscope, and a scanning electron microscope. The video camera recorded 32 frames/s, each with an imaging time of 1/2000 s. Combustion photography was employed for measuring the burning rate. Burning rates of both sandwiches and propellant-type samples were taken after a steady-state profile had been developed. The tests were run at pressures of 2.07, 3.45, and 6.89 MPa. The test plan was to have at least two experiments yielding two independent measurements for each test condition. The burning rate was determined by the data collected in the form of position vs time from the video pictures (minimum 5 points), and a least-square linear fit was used to decide the burning rate. The average burning rate of these two (or more) experiments was calculated to obtain a data point corresponding to a particular matrix thickness at a specific pressure. In cases of poor reproducibility, three (or more) tests were sometimes run.

Table 1 Summary of experimental conditions

Combustion photography for burning rate
Pure binder sandwiches
AP-filled sandwiches with 10-μm AP in the binder
AP-filled sandwiches with 33.5-μm AP in the binder
1) Range of matrix thickness: 125–600 μm
2) AP-binder matrix material
Mass ratios of AP:PBAN binder = 5:5 and 7:3
AP particle size: 10 and 33.5 μm
3) Test pressure: 2.07, 3.45, 6.89 MPa
Quench burning, SEM of the samples
1) All pressure-matrix conditions notes above
2) Matrix lamina thickness chosen to correspond to thin, thick, and one or two intermediate thickness near maxima of burning rate vs matrix thickness curve

Interruption of burning by rapid depressurization permits better resolution of the burning surface details than is possible in the combustion photography. Results from the combustion photography tests were used to choose appropriate delay times after ignition to assure quench after a steady-state surface profile was reached. The quench was accomplished by venting the test chamber with a burst diaphragm. The quenched surface was examined to collect information on surface profile, the oxidizer-fuel laminae interface region, and AP particles in matrix laminae, using an optical microscope and a scanning electron microscope. The matrix thicknesses that were used in quench tests were chosen to correspond to points on the burning-rate curves that seemed most important (see Table 1).

Experimental Results

The results of burning-rate tests are shown in Figs. 3 and 4. Figure 3 is for 5:5 matrix materials. This very fuel-rich material would not sustain burning when tested as propellant-type samples. Figure 4 is for 7:3 matrix material. The burning rate of the material when burned on its own is marked by lines on the right-*y* axis. In each of these figures the burning rates are shown as functions of matrix lamina thickness, for each particle size and three pressures. Marks on the left-*y* axis show the AP self-deflagration rate.

Figure 5 shows the surface profiles of the sandwiches under selected conditions indicated in the figure. The differences in profiles under different conditions are used to help reconstruct the corresponding flame structures and identify the part of the flame that dominates the sandwich burning rates. The profile has an overall concave shape if the sandwich burning rate is higher than the AP self-deflagration rate (typical of low pressure). If the matrix burned very fast on its own, the matrix surface would be expected to get progressively further ahead of the rest of the surface. This did not happen for the conditions tested here.

Scanning electron micrograms of selected quenched sandwiches are shown in Figs. 6–12.

1) The surface of the AP laminae had the same froth, depressions, and ripples on the AP surface (typical of AP self-

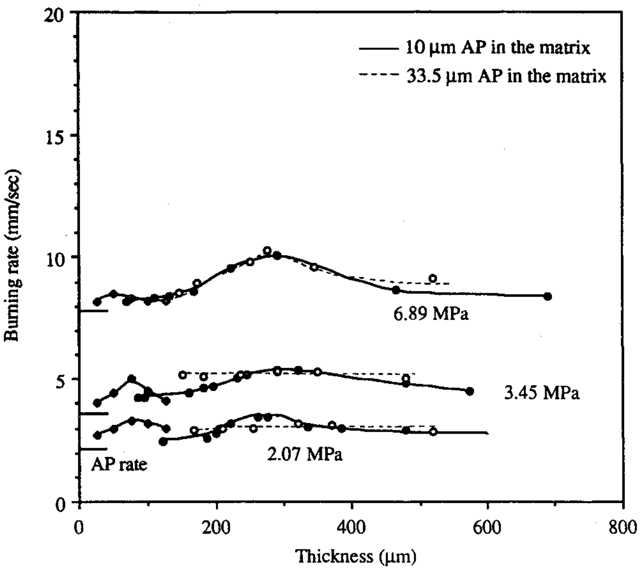

Fig. 3 Burning rate of 5:5 sandwiches.

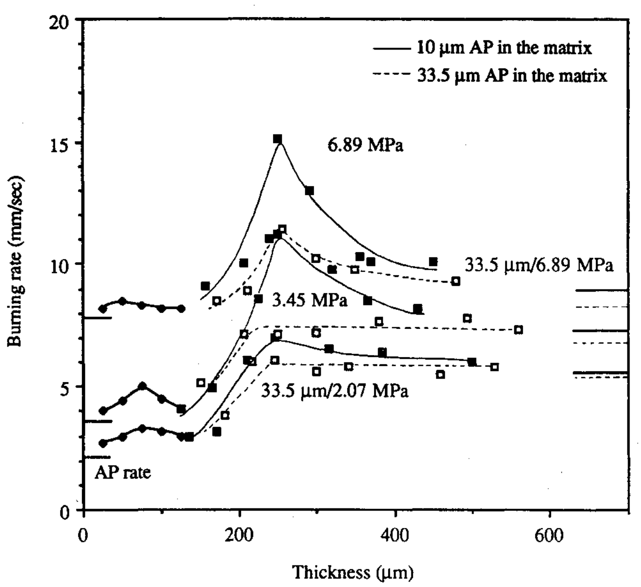

Fig. 4 Burning rate of 7:3 sandwiches.

deflagration) as in other sandwich burning tests with pure binder laminae (without AP in the binder).[1-4]

2) AP surface areas along the AP-binder contact interface exhibited a smooth surface. This region almost always "protrudes," in the sense that the leading point of the AP profile occurs 25–50 μm out from the AP laminae-matrix contact plane similar to sandwiches with pure binder laminae (Figs. 5 and 9).[1-4]

3) The "smooth band" extends out approximately to the leading-edge point (Figs. 5 and 6). The band was very irregular with the coarse AP matrix at higher pressures (Fig. 7), with the irregularities often relatable to the proximity of adjoining matrix particles.

4) Conditions that gave the highest burning rates resulted in narrow smooth bands with little "protrusion" of AP at the interface plane (Figs. 5 and 8).

5) The matrix surfaces were usually recessed slightly relative to the AP laminae, and appeared to have been dominated by a binder melt (especially with 5:5 mass ratio). The fine-AP particles appeared to be covered by binder, although many were revealed as smooth "bumps" (Fig. 9).

6) Coarse AP particles in the matrix were often visible (especially at higher pressure and/or 7:3 mass ratio), usually recessed in surface depressions (in 6.89-MPa tests). The ma-

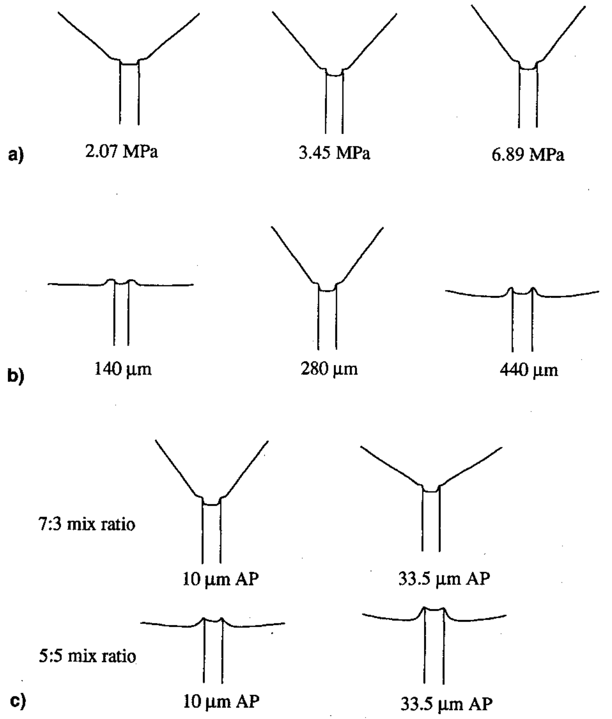

Fig. 5 Examples of burning surface profiles: a) profiles at maxima of burning rate vs matrix thickness, b) profiles at different matrix thickness at 6.89 MPa (10 μm and 7:3 mix), and c) profiles at maxima of burning rate vs matrix thickness curves at 6.89 MPa.

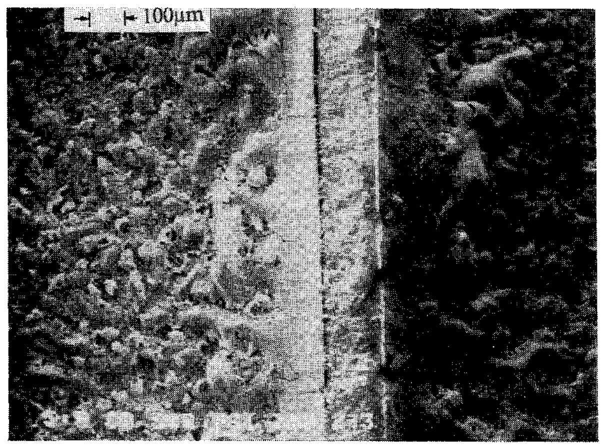

Fig. 6 Quench surface of a 5:5 (10 μm) AP-filled sandwich at 3.45 MPa.

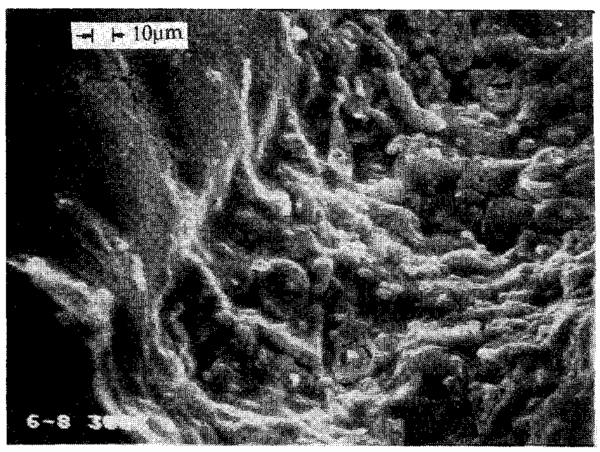

Fig. 7 Quench surface of a 7:3 (33.5 μm) AP-filled sandwich at 6.89 MPa.

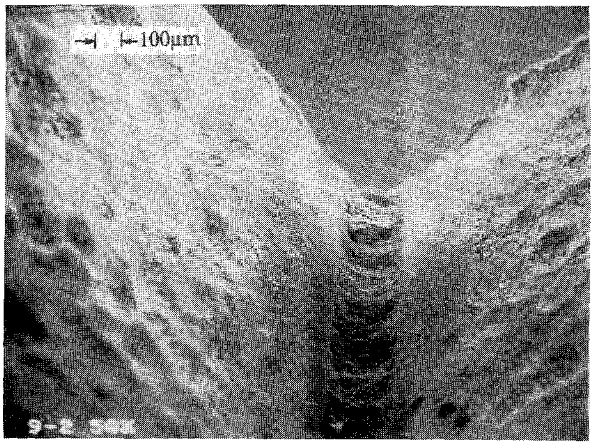

Fig. 8 Quench surface of a 7:3 (10 μm) AP-filled sandwich at 2.07 MPa.

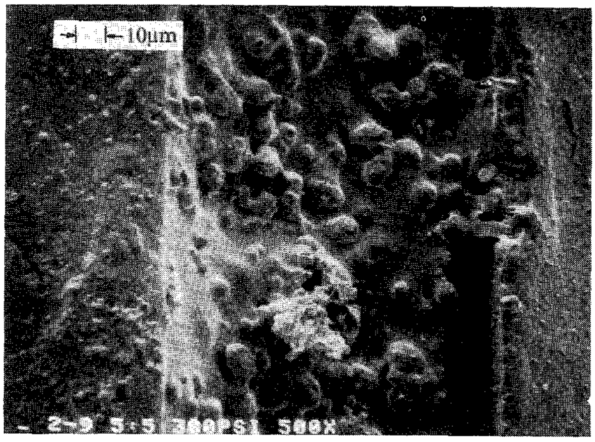

Fig. 9 Quench surface of a 5:5 (10 μm) AP-filled sandwich at 2.07 MPa.

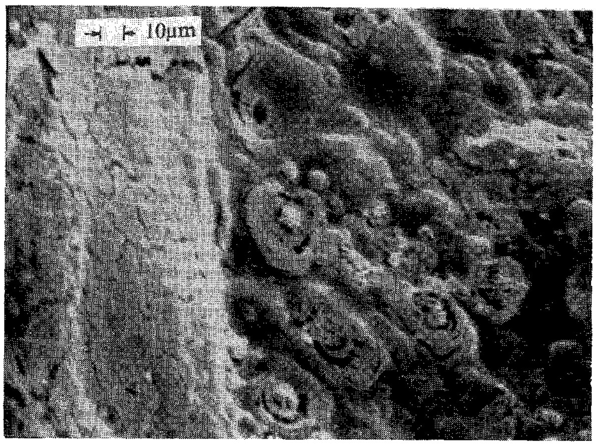

Fig. 10 Quench surface of a 8:2 (33.5 μm) AP-filled sandwich at 6.89 MPa.

trix surfaces had a cellular quality with AP particles visible in the bottom of cells. Some depressions were empty, apparently left by burned out AP particles (Figs. 10 and 11).

7) Under conditions where some AP particles are exposed (and appear to have been burning independently), such particles were more numerous in the part of the surface immediately adjoining the AP laminae (Fig. 12).

8) The quench tests on sandwiches with 8:2 ratio in the matrix laminae showed a somewhat drier surface, but otherwise looked like the corresponding results with 7:3 matrix (Fig. 10).

Considerations Involved in Discussion of Results

For sandwiches with pure binder laminae, the flame complex consists of an AP self-deflagration flame over most of the AP laminae, except at pressures below the AP self-deflagration limit.[2,7] The oxidizer-fuel diffusion flame originates in the AP-binder vapor mixing region above each AP-binder contact line on the surface. The LEFs stand off from the surface at sites where heat losses and heat release are in balance, to give a local flame with flame speed sufficient to be stationary in the outflowing gas (Fig. 1). The size and location of LEF is dependent on the accumulation of premixed reactants, chemical reaction rates, and hence on pressure or presence of diluents. Beyond the LEF, the diffusion flame extends outward in the flow until one or both reactants are consumed, usually at a closure between the two diffusion-flame sheets over the matrix lamina, because the sandwiches are oxidizer rich. It is important to note that the LEF is an intense premixed flame, close to the surface, with characteristics very different from the outer diffusion flame.[7] In this article these LEFs will be called lamina leading-edge flames or "LLEFs," to distinguish them from similar flames that occur above the AP particles when conditions permit (larger particles and/or higher pressures). The particle LEFs will be referred to here as "PLEFs." In Fig. 13, the two LLEFs burn independently of each other in sandwiches with pure binder laminae that were thick, while their interaction becomes important when they are close together (thin binder). The effect of binder lamina thickness on burning rate is due primarily to this LLEF interaction, indicating the importance of the local nature of the action of LLEFs and the importance of interactive behavior.[2,5–7] In this article, this interpretation must be extended to the presence of PLEFs and the possible interaction of PLEFs with other PLEFs and with adjoining LLEFs. The interactions occur when the flamelets are effectively competing for the same reactant and heat supplies through multidimensional diffusion of heat and reactants.

AP particles used in the matrix in this study may have fully developed flame complexes of their own (Fig. 2), but the earlier sandwich-burning studies[2] suggested that conditions for such flames would not be satisfied for the samples used here except with the larger particles at high matrix loading (i.e., 7:3), at high pressure. The reasoning is as follows: the LEF centers on the stoichiometric surface of the mixing fan that develops above the AP/binder contact line on the surface. The particles are in a locally fuel-rich environment, so that the stoichiometric surface closes at a "tip" above the AP particle (Fig. 2). At low pressure, the LEF stands far out on this stoichiometric "tent." If the particle is small (short tent) or the pressure is low (large PLEF standoff), the PLEF may be clear out at the tip. Further decreases in particle size or pressure tend to force the PLEF to a location beyond the tip. However, in this region there is no stoichiometric point; conditions are fuel-rich, and increasingly so at further distances from the surface. This situation is not conducive to a stable PLEF because the flame temperature decreases when the PLEF moves outward to find a stable heat-loss, heat release condition. In pure binder sandwiches these conditions led to quenching of the LEFs,[2] and it is expected that this will happen to PLEFs also when the exposed AP area is small, the pressure is low, and/or the local mixture ratio is more fuel-rich. This argument is supported not only by qualitative theory, but also by sandwich burning results,[2] and by the combustion behavior of bimodal AP propellants.[8] In the presence of still-attached LEFs on neighboring larger particles or AP laminae, the areas of fine particles on the surface continue to pyrolyze, and it is postulated that the resulting AP/binder vapor mixture forms a premixed "canopy" flame further from the surface (Fig. 14), probably piloted by the attached LEFs still present on the larger particles or laminae. In a limiting case of very fine AP particles, the AP vapors produce a mixture that behaves in the lamina mixing fan as a diluted fuel, but behaves

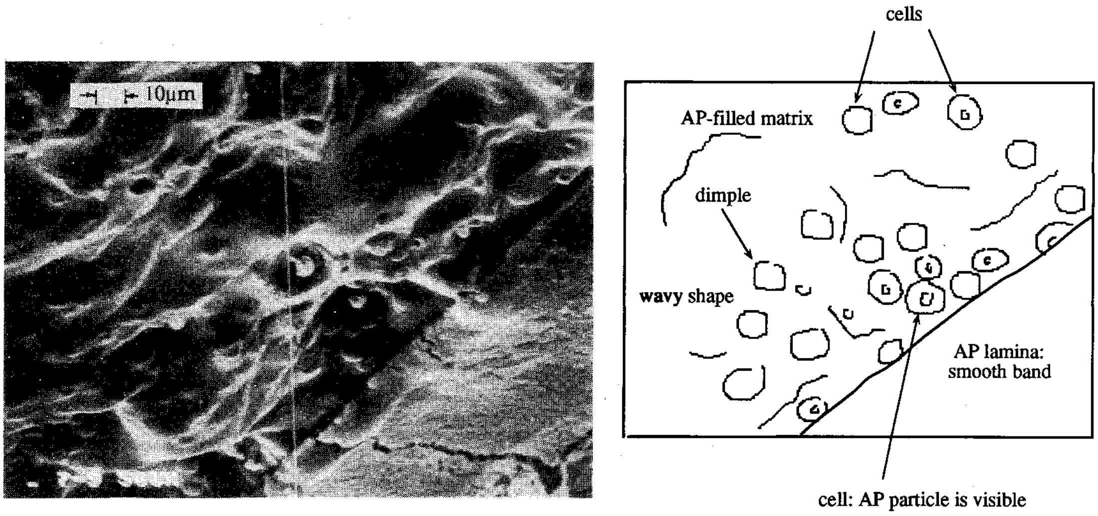

Fig. 11 Quench surface of a 5:5 (33.5 μm) AP-filled sandwich at 6.89 MPa.

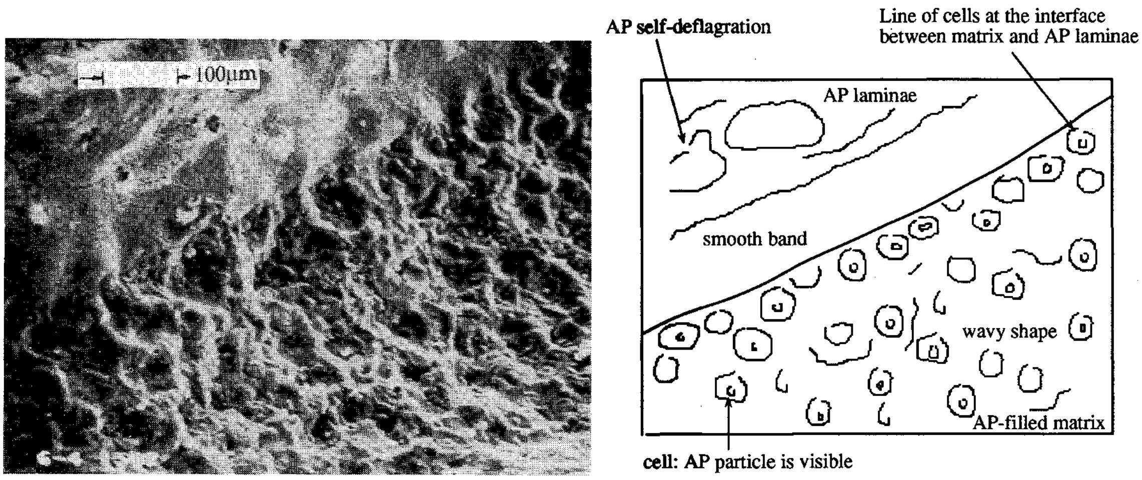

Fig. 12 Quench surface of a 7:3 (33.5 μm) AP-filled sandwich at 6.89 MPa.

as a premixed O/F system when the LLEF is reached. This behavior is enlarged upon in the following section.

Discussion of Results

The discussion of results is shown below as a series of statements about the combustion zone structure and processes. The first five statements were developed in studies of combustion of sandwiches with pure binder laminae,[1–4] but are applicable to the present results with AP-filled matrix laminae as well. The subsequent statements pertain to further observations and interpretation pertinent to AP-filled matrix laminae (in the range of variables studied).

1) The burning rate of the sandwiches is determined by the regression rate at the leading point of the AP surface, and hence by the heat flow to, and heat loss from that location. This generalization results from the fact that the AP contributes its own exothermic reactions to the heat balance, and the fact that the LLEF is usually centered over the AP surface because the stoichiometric surface in the mixing fan is located there due to the relatively dilute oxidizer species concentrations in the AP vapors and products (Figs. 1 and 14b).

2) With thick binder laminae, the two LLEFs do not interact, and vapors from the center part of the matrix flow away between the LLEFs without near-surface exothermic reaction. The lateral heat flow to this "excess" fuel in the solid and gas phase represent a heat drain from the rate controlling site in the AP surface (Fig. 13a). The binder lamina protrudes in the middle where heat sources are relatively distant.

3) With intermediate binder lamina thickness, the LLEFs interact to form one flame (the entire species and heat diffusion fields interact). The loss effect in 2 is minimized, leading to higher flame temperatures, reduced standoff distance from the condensed surface, and correspondingly higher burning rate at the leading edge site (Fig. 13b).

4) For still thinner binder laminae, the coupled LLEFs are fuel-deficient, so that the overall heat release is low. The lateral heat loss from the leading-edge sites to the rest of the AP lamina(e) becomes increasingly important because of the decreased net heat flux, and the burning rate is lower. In the limit as the binder thickness approaches zero, the burning rate falls to the AP self-deflagration rate (Fig. 13c).

5) A phenomenon described here as "LLEF detachment" occurs at some finite low binder thickness for which the LLEFs are no longer stable in the mixing flow, because there is no location where heat release can match the needs for a flame with speed equal to the outflow speed. The sandwich rate is presumably equal to the AP rate below this limit, but is not well verified because test samples of good quality are difficult to fabricate at these low binder thicknesses (this condition would determine the approach of the burning-rate curves to the AP rate at the left in Figs. 3 and 4).

To interpret the effects of granular AP in the binder lamina, the following arguments will be added to the above list.

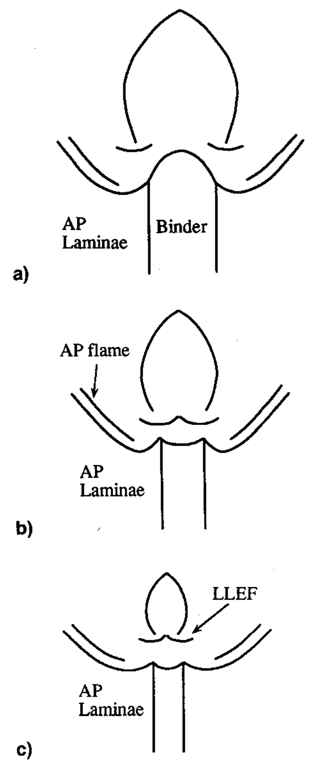

Fig. 13 Dependence of flame complex for AP-binder-AP sandwich on binder lamina thickness: a) thick binder (>125 μm), b) intermediate binder, and c) thin binder.

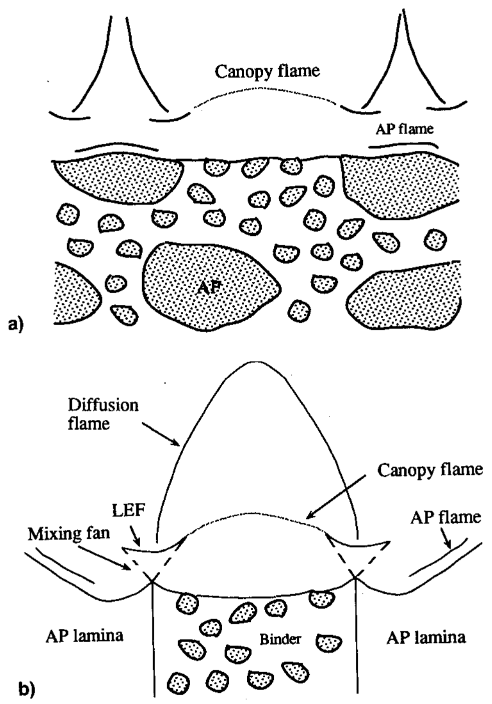

Fig. 14 Flame complex in systems with bimodal AP size distribution not supporting attached flames on individual particles: a) propellant with coarse and fine AP and b) sandwich with fine AP in the binder lamina.

6) One effect of AP in the binder is dilution of the fuel, which will shift the stoichiometric surface and leading edge of the LLEF toward the matrix lamina (Fig. 15).

7) A second effect of AP in the binder is to extend the fuel-rich side of the LLEF further toward and over the binder lamina because of the presence of oxidizer enrichment there (Fig. 15).

8) A third effect of AP relates to the extent of mixing of the AP particle vapors with the fuel vapors by the time they reach the LLEF locations. With fine AP particles or large LLEF standoff (low pressure), mixing can be complete. With coarser AP, the mixing may be incomplete, with mixing fans around larger exposed particle surfaces, extending out to and beyond the LLEF standoff distance.

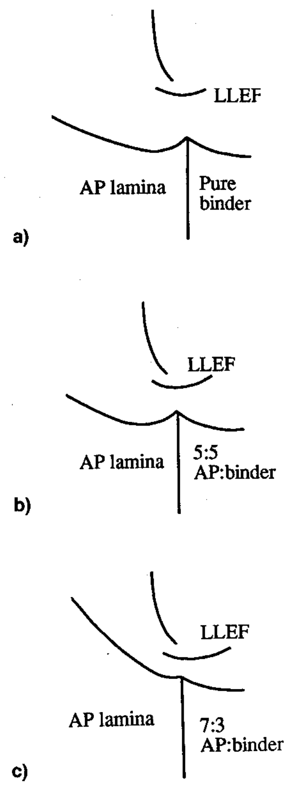

Fig. 15 Effect of fine AP to the binder lamina: a) narrow LLEF over AP lamina; b) wider LLEF, stoichiometric point close to the surface and shifted toward lamina contact plane; and c) wider LLEF, stoichiometric point over outer edge of AP lamina, LLEF extends well over matrix lamina.

9) The larger AP particles may have their own attached particle LEFs (PLEFs), particularly at high pressures.

In order to make an interpretation of results, attention will be focused on the burning-rate trends, and the surface profiles and surface details will be used to test or complete the mechanistic arguments. The strategy will be to compare the burning rate curves with different amounts of AP, different size particles, and different pressures, and construct arguments to explain the differences based on the nine contributing effects listed above. When these arguments, qualitative theory, and the secondary evidence are all reconciled, a fairly detailed picture of the combustion behavior emerges. At the outset it is helpful to note some features that were common to all or most of the results.

1) The sandwich rates were all higher than the AP self-deflagration rates, but decreased toward the AP rate at the low end of the lamina thickness range. This positive slope region of the rate vs thickness curves occurred over a larger lamina thickness range with AP in the matrix. Recalling item 4 above, this presumably reflects the effect of a more dilute fuel (item 6), which extends the fuel-deficient region to greater lamina thickness.

2) The sandwich profiles were all more or less "V" shaped, to a degree consistent with the ratio of the sandwich rate to AP self-deflagration rate, establishing that the rate is controlled by the local flame complex involving the lamina interface region. Some protrusion of the AP/binder matrix lamina at its center occurred with thick 5:5 matrix laminae (i.e., the matrix does not control the rate). Nearly flat AP profiles occurred in some tests at high pressure, indicating that the AP rate is almost rate-controlling at higher pressure. There was no evidence of interfacial burning between laminae.

3) Under nearly all conditions the detailed profile of the AP lamina in the region near the lamina contact plane was concave upwards, with a leading edge at some tens of micrometers from the contact planes, and with a region of retarded AP regression and smooth surface closer to the contact plane. As in the interpretation of results with pure binder laminae,[2] this supports the interpretation in no. 2, and indicates that heat loss by conduction from the AP to the matrix lamina is occurring, and the LLEF is still centered over the AP. A possible exception was with test conditions that gave the highest burning rate, with the 7:3/10-μm matrix, where the leading edge of the AP was a ledge at the interface plane (Figs. 5a and 8).

4) The matrix laminae were recessed relative to the adjoining part of the AP laminae, with slight protrusion in the middle of some thick laminae. This is similar to results with pure binder laminae,[2] and is believed to result from the lower pyrolysis temperature of the binder (compared to the AP). Protrusion in the center (no. 2 above) is an indication that the matrix burning does not control the sandwich burning rate, and that interlamina heat transfer and/or the LLEFs contribute to pyrolysis of the matrix surface nearest to the AP laminae.

Turning now to comparisons of burning rate vs matrix thickness curves, the addition of AP shifted the maximum of the rate curves to a higher lamina thickness, an effect of fuel dilution (no. 6 above). It also gave higher burning rate (except in the fuel-deficient thin binder domain), an effect (no. 7 above) of greater width of the LLEFs because of premixed AP vapor in the fuel flow (and hence, less lateral heat loss, higher LLEF temperature). In the case of the 7:3 mixture, the asymptote at high matrix thickness is particularly high because the matrix burning rate is considerably higher than the AP rate. However, it is important to note that 1) the rate is higher than matrix rate under most conditions, indicating cooperative interactions of the LLEF and the matrix "canopy" flame (Fig. 14); 2) the matrix lamina never runs on ahead of the AP, indicating that the matrix-assisted LLEFs control the rate via the leading edge in the AP; and 3) the rate peaks at intermediate lamina thickness, further supporting the interpretation in 2) that it is the LLEF that controls rate, and the matrix exerts a rate depressing effect as a heat sink for heat flow from the rate controlling site in the AP lamina (this heat drain is reduced at lower lamina thickness, allowing higher rate until the fuel deficient domain is reached).

In summary, the mechanistic effect of addition of AP to the binder lamina is to give a more dilute fuel flow that extends the fuel deficient thin-lamina region to higher lamina thickness, and shifts the stoichiometric surface of the lamina mixing fan (and hence the leading edge of the LLEF) toward the lamina contact plane. At the same time, the presence of the AP vapor mixed with the fuel from the matrix surface extends the fuel-rich side of the LLEF, yielding more net LLEF heat release (except in the fuel deficient thin binder domain), with increased heat flow directly to the interface region and matrix lamina. In the domain of parameters tested, the maximum burning rate is higher with more AP addition, consistent with the above interpretation.

Comparing the burning rate curves for 10- and 33.5-μm particles, the rate is higher for 10-μm particles under almost all conditions. This is consistent with the thesis that the premixed vapors are more fully reacted in the LLEF, supporting heat flow to the rate controlling site, and probably reducing lateral heat drain from that site by more effective direct heating of the matrix lamina. This is supported by the observation that the rate of the 7:3 matrix alone is higher for 10-μm AP than for 33.5-μm AP.

It is notable that the peak in the burning rate curve with 7:3 matrix (Fig. 4) is more conspicuous with fine AP than with coarse AP, further supporting the interpretation that more complete mixing at the level of the LLEF gives greater extension of the LLEF on the fuel-rich side, and greater shift of the stoichiometric surface. The AP/binder vapors appear to be almost completely premixed at the LLEF height with 10-μm AP, whereas the 33.5-μm particles probably have stoichiometric tips near the LLEF height (higher than LLEF height at 6.89 MPa, less than LLEF height at 2.07 MPa). The large particles appear to have PLEFs at 6.89 MPa, and to a limited extent at 3.45 MPa, presumably partially compensating for the incomplete mixing to give a peak in the rate curve. The presence of PLEFs is also indicated by the quenched samples, which show exposed AP surfaces in the matrix (Figs. 7, 10, and 12). The number of such particles is higher along the contact plane, indicating cooperative support by the LLEF, and oxidizer enrichment by diffusion from the AP lamina outflow (a complex three-dimensional diffusion field). This coupled behavior between the lamina burning and the particle burning is indicated by the irregular edge of the AP lamina that was manifested only under these conditions (7:3, 33.5 μm, 6.89 MPa, Figs. 7 and 12) and absent under other conditions.

The mechanistic effect of particle size on burning rate is alluded to above, but merits focused comment. Fine particles appear to vaporize endothermally (presumably by dissociative sublimation to NH_3 and $HClO_4$), and the vapors diffuse into the surrounding flow of fuel vapor (fuel rich) before appreciable heat release. A premixed flame can then occur, which would give the observed matrix rate (zero in 5:5 mixtures, higher than the pure AP rate with 7:3 mixtures, see Fig. 4). However, the sandwich rate is higher than the matrix rate under most conditions, indicating a cooperative effect between AP self-deflagration and matrix burning that has been described above as governed by matrix vapor enhancement of the LLEF and resulting enhancement of the heat balance at the leading edge of the AP lamina profile. When coarser AP particles are used in the matrix, the matrix rate is reduced because the oxidizer/fuel (O/F) mixing takes longer (i.e., is not complete at LLEF height). The sandwich rate is reduced for the same reason. However, the nature of the matrix flame changes to a particle flame complex as pressure and particle size increase, a flame complex that is an array of three-dimensional particle flames is analogous to the two-dimensional sandwich flame. For the coarser AP particles used here, this change was apparently 1) fully developed only at 6.89 MPa and 2) significantly aided locally adjoining the AP lamina where additional oxidizer vapors and lateral heat flow were available. However, this enhancement of PLEFs did not enhance the sandwich burning rate as much as the premixed O/F flow to the LLEF provided by the fine AP matrices.

The mechanistic effect of pressure is primarily facilitation of a faster gas phase reaction rate at higher pressure, resulting in establishment of LLEFs and PLEFs and canopy flames closer to the surface. This effect is included in almost all combustion models, but the present results indicate the effect in a much more complicated framework because it involves all three kinds of flamelets, acting locally and interactively, and with the possibility of absence or presence of the canopy flames and PLEFs depending on pressure, particle size, and AP/binder ratio in the matrix. In propellants with multimodal AP size these local effects may, under some circumstances, average out in time, allowing the conventional one-dimensional form of the energy equation. However, the conditions for applicability of that assumption need to be re-examined, and provisions are needed for including the pressure-dependence, i.e., of PLEFs and canopy flames. The one-dimensionalization of the energy equation seems to be particularly inapplicable for modeling oscillatory response of combustion.

Summary

It has long been understood that the combustion zone of a composite propellant consists of three-dimensionally complex microscopic structures.[9,10,12,13] In order to develop useful analytical models that are mathematically tractable, it is necessary to determine what features of this complex process dominate the steady and nonsteady burning. Since the dominant processes differ over the range of particle sizes, pressure and mixture ratio, one must either tailor the model to limited conditions or be sure that it is complete enough to reflect the dominant processes and correctly reflect the range of conditions of interest, while excluding unnecessary detail that burdens the model and computational requirements. The present studies provide many mechanistic insights needed for realistic phenomenological modeling, and has motivated more rigorous modeling of the oxidizer-fuel flames.[7,11] Some of these insights were suggested from earlier sandwich burning studies and propellant combustion models,[1-13] and are simply validated by the present study. But the study does more. It starts the job of sorting out what mechanisms are important under what conditions. It identifies conditions under which premixing of oxidizer and binder vapors gives a premixed "canopy" O/F flame, and conditions under which the flame structure is not premixed and is three-dimensionally complex. It shows that these extremes of behavior can both be present at different sites on the same burning surface, and that coupling behavior between such sites can be a significant factor in burning rate. It shows details of the process by which, as proposed by Summerfield,[12] the control of burning is "handed over" from kinetic control at low pressure to diffusion control at high pressure, and shows that, as proposed by Beckstead et al.[9] and Cohen,[10] control is never fully handed over to diffusion control because of the persistent importance of a kinetically limited leading edge of the diffusion flame at high pressure. Coupling of adjoining flamelets, proposed in some propellant combustion models,[13] is shown to be real, and details of the process are proposed based on high resolution studies of quenched samples and interpretation of sandwich burning rates.

While extension of the enhanced understanding of the combustion details to practical application was beyond the scope of this study, there is obvious potential for application to tailoring burning characteristics, and for improvement of modern burning rate and combustion response models.

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