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ABSTRACT

A preliminary experimental investigation was carried out to investigate the ignition of ultra-fine aluminum (UFAl) compared to conventional sized aluminum (CSAl) particles in ammonium perchlorate (AP)-polybutadiene acrylonitrile acrylic acid (PBAN) solid propellants. To evaluate the temperature criteria for igniting UFAl, matrix samples (binder, fine AP and Al only) were prepared with various loadings of 10μm fine AP (fAP) as a means of varying the AP-binder flame temperature, and with Al coarse-to-fine ratio of 0(30μm)/20(UFAl) and 80(30μm)/20(UFAl). Preliminary results showed that UFAl sized particles ignite at lower gas-phase flame temperatures than CSAl particles and that the UFAl particles tend to affect the combustion processes close to the propellant surface depending upon the availability of oxidizer.

INTRODUCTION

In recent studies of ultra-fine aluminum (UFAl~0.1μm) in ammonium perchlorate (AP) solid propellants with bimodal AP (10μm:400μm and 82.5μm:400μm) and bimodal aluminum (Al) distribution (30μm:UFAl), the burning of UFAl was found to create a very dense aluminum burning region (ABR) directly above and some distance beyond the propellant surface (~3000-4000μm) compared to the burning of conventional sized aluminum (CSAl~12-100μm).[1-3] The density of the ABR was found to be the product of the number of burning Al particles/droplets/agglomerates leaving the propellant surface per unit area (one 30μm Al particle is the mass equivalent of 10^7 UFAl particles), which is very dependent upon the propellant microstructure (see later). The combustion of fine Al (~3μm) and UFAl particles occur much closer behind the AP-binder flame because of their near equilibrium state with the gas flow (temperature & velocity) compared to CSAl. As a result, they ignite quickly as they pass through the flame surface and burn close behind the convoluted flame canopy. This dense luminous bright ABR was found to be responsible for a significant amount of heat feedback to the propellant surface and to the AP-binder flame array in the form of either radiation and/or conduction, which resulted in high burning rate propellants.

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As mentioned earlier, the ability to create a dense ABR was found to be very dependent upon the propellant microstructure, the availability of oxidizer species for the Al and upon the ability to ignite the UFAl close to the propellant surface through appropriate ignition sites. These necessary ignition sites were provided through the complex AP-binder flame array: the Leading Edge Flame (LEF), its outer diffusion flame, and the matrix (that portion of the propellant consisting of binder and fine AP (10μm) only) flame.[4] From recent studies of varying the AP coarse-to-fine (AP c/f) ratio for bimodal aluminized propellants, the experimental results suggested that an enhanced (or hotter) matrix flame had the ability to ignite UFAl sized particles at lower temperatures than typical CSAl particles.[1-3, 5]

To test this hypothesis, a systematic study was carried out on varying the oxidizer-to-fuel ratio of a matrix-based propellant with monomodal (UFAl) and bimodal (UFAl: 30μm) Al distributions. The study includes comparisons of the burning rates and the ABR's of propellants to its corresponding matrix mixture. The paper represents a preliminary study addressing in detail the overall criterion for Al ignition as it relates to CSAl and UFAl. This will involve issues such as the breakdown of the protectiveness of the Al oxide coating and the inflammation of the Al particle/ agglomerate as it relates to finer Al particle sizes. In addition, the proximity and the temperature of the AP-binder flamelets to the propellant surface and to the Al will also be addressed as it pertains to UFAl ignition. Finally, the global effects of the intensity and density of the UFAl flame will also be discussed with respect to the overall combustion mechanisms of aluminized solid propellants.

Aluminum Ignition

The ignition of CSAl either as single particles or within a propellant has been studied extensively in the past.[6] This section highlights the mechanism involved with Al ignition in order to give the reader a fundamental understanding.

The Al particles have a very thin protective oxide skin (Al_2O_3), which inhibits the ignition of the Al particles/agglomerates. The oxide coating of a typical CSAl, for example 30μm, represents approximately 0.5% of the particle's mass with the remaining 99.5% representing the Al fuel.[1,7] During particle heat up, the Al melts (melting temperature 660°C) much earlier than the oxide skin (melting temperature 2047°C) which encapsulates the Al. The ratio of the thermal expansion coefficient of the Al to that of the oxide is greater than 1. The volume expansion of the Al (6% upon melting) is sufficient to push through the oxide skin. This causes cracks in the oxide shell to occur, thus initiating a process of Al leaking. The exposure of the Al fuel to a chemically reacting and thermally high temperature environment initiates the process of diffusion between the fuel and the oxidizer and thus with the chemically high temperature environment sustains a chemical reaction. During the Al residence on the propellant surface, there is a sudden increase in the droplets luminosity, which is evidence of particle heat up and reactions. During this time, the Al starts evaporating and mixing occurs between the Al fuel and oxidizer. When an appropriate mixture ratio is attained and high enough temperatures are reached to sustain a chemical reaction, the Al droplet ignites and a detached flame envelope is established around the droplet. Generally, the ignition of Al particles can either occur near the propellant surface (provided it is hot enough and sufficient diffusion occurs), near a LEF, or near a diffusion flame. For the case of LEF based ignition, the likelihood of the Al particles/agglomerates being near an LEF depends upon the microstructure packing arrangement.[1,6,7]

Al particle liftoff is attained by the progression of inflammation through the accumulated particles towards the propellant surface, hence encouraging the process of propellant pyrolysis and reducing the effects of surface tension. This eventually encourages particle/agglomerate liftoff and given the appropriate temperature conditions, the Al particles/agglomerates ignites. The time spent during particle heat up, diffusion time and reaction time is commonly referred to as the ignition time delay.[1,6] However, the ignition of Al is typically a series of progressions rather than a discrete event in time. This starts from the moment of Al exposure on the propellant surface, where the Al begins its complicated process of accumulation/concentration-sintering and agglomeration.

As a result, this paper represents a preliminary study specifically addressing the temperature criteria of the AP-binder flame needed to attain UFAl ignition or a ‘runaway event’ compared to CSAl.

Propellant Formulation

All propellants had a mass loading of 11% binder, 71% ammonium perchlorate (AP) and 18% aluminum (Al). The 11% binder loading was composed of the following: PBAN-Prepolymer 63.18%, Dioctyl Adipate (plasticizer) 15.78% and Epoxy Curing Agent 21.04%. The size of the coarse AP and fine AP were 400μm and 10μm respectively. The AP coarse-to-fine (AP c/f) ratio was varied during the investigation, as well as the Al coarse-to-fine (Al c/f) ratio. The size of the coarse and fine Al particles were 30μm (Valimet Metalurgical-H30) and ~0.1μm (Argonide-Alex) respectively.[1,3,8] The matrix based propellants (i.e., in this particular case the portion of the propellant consisting of binder, Al and fine AP (10μm) only) were equivalent to the binder, the coarse Al (cAl: 30μm), the ultra-fine Al (UFAl: ~0.1μm) and the fine AP loading of the above propellants, see Table 1 below.

PBAN Formulation			
Mix #	**Loading**	**Propellant**	**Matrix**
12	**AP c/f**	**80/20**	***N/A***
	Al c/f	**80/20**	***N/A***
27R	**AP c/f**	***N/A***	**0/20**
	Al c/f	***N/A***	**0/20**
30	**AP c/f**	***N/A***	**0/20**
	Al c/f	***N/A***	**80/20**
25	**AP c/f**	**60/40**	***N/A***
	Al c/f	**80/20**	***N/A***
28	**AP c/f**	***N/A***	**0/40**
	Al c/f	***N/A***	**0/20**
31	**AP c/f**	***N/A***	**0/40**
	Al c/f	***N/A***	**80/20**
26	**AP c/f**	**50/50**	***N/A***
	Al c/f	**80/20**	***N/A***
29	**AP c/f**	***N/A***	**0/50**
	Al c/f	***N/A***	**0/20**

Table 1: Summary of the Mass Loadings of the Propellant and Matrix Formulation.

Experimental Technique

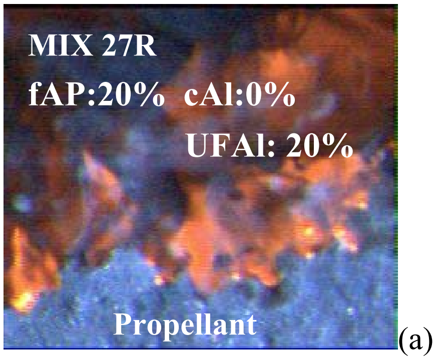
High-speed digital combustion imaging was used in measuring the burning rate of both the propellant and matrix samples. The burning rates were measured from 1.38MPa to 6.9MPa. The high-speed combustion images were also used to analyze the ABR. Further details of this experimental arrangement can be found in references 1-3 and 8. All propellants and matrix samples were machine mixed for approximately one hour and vacuum pressed for approximately 15-20 minutes. Details of the mixer and vacuum degasser can be found in reference 1.

Experimental Results

Combustion Images of the Matrix

A qualitative discussion of the propellant's ABR with a reduction in the Al particle size (monomodal Al distribution: 30µm, 15µm, 3µm and UFAl) and Al c/f (30µm:UFAl) ratio was discussed extensively in reference 1-3 and 8. It concluded that propellants with CSAl particles (30µm and 15µm) showed a less luminous and segmented ABR, while propellants with 3µm and UFAl gave a very luminous dense ABR more so with UFAl particles. Propellants with bimodal Al distribution (30µm:UFAl) showed a dense luminous ABR was attainable with only 20% UFAl (Al c/f 80/20) i.e., 3.6% of the total 18% Al loading.

Figure 1 shows the combustion images of the matrix-based samples (see Table 1) with Al c/f ratio of 0/20 and 80/20 at various fAP mass loadings i.e., 20%, 40% and 50% of the total 71% AP loading.



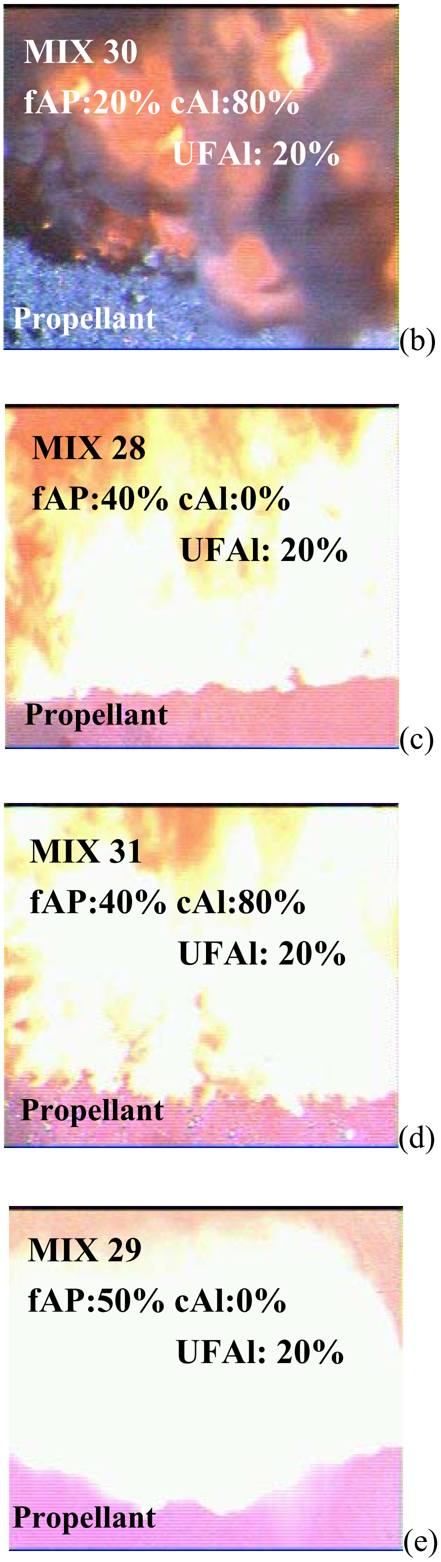
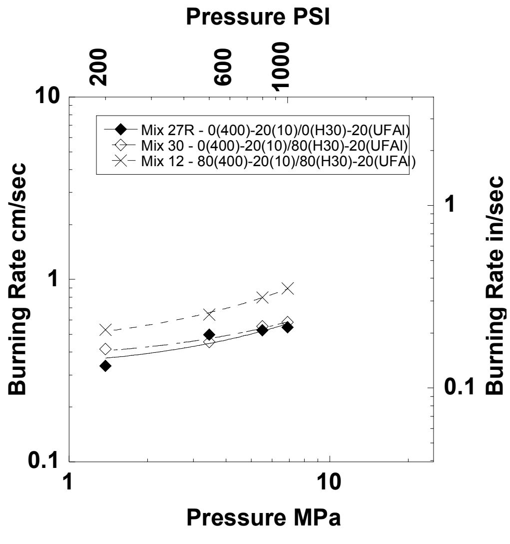


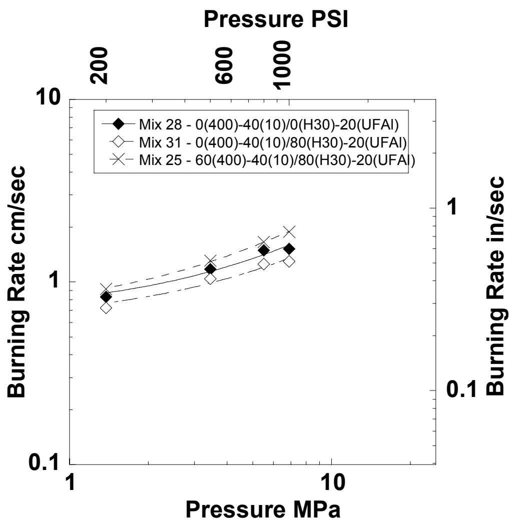
Figure 1: Images (~3mm high) of the combustion zone at 6.9MPa of the matrix based propellant with various mass loadings of fAP, cAl and UFAl.

Figure 1a and Figure 1b show the combustion zone of the matrix sample with an Al c/f ratio of 0/20 and 80/20 respectively, and a fAP loading of 20%(10μm); i.e., 14.2% of the total 71% AP loading. The combustion images showed a ‘dull orange to yellow’ ABR (no presence of intense luminosity), indication of the AP-binder flame and the ABR being ‘overly’ fuel rich with its consequently blackbody continuum radiation. Figure 1c and Figure 1d show the combustion zone of the matrix sample with Al c/f ratio of 0/20 and 80/20 respectively with a fAP loading of 40%. The images show the existence of a dense luminous ABR with the slight presence of coloration in the dull orange to yellow range. Further increases in the fAP loading to 50% show a fully luminous dense ABR; see Figure 1e.

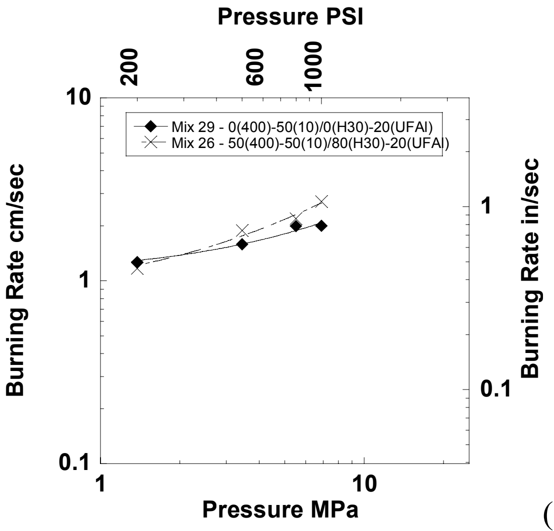
The Effects of the Matrix Flame on the Ignition of UFAl



(a)



(b)



(c)

Figure 2: The burning rate effect of propellants and matrix samples as a function of pressure at Al c/f ratio of 80/20 & 0/20 and AP c/f ratio: (a) 0/20 & 80/20; (b) 0/40 & 60/40 and (c) 0/50 & 50/50.

In an effort to determine the temperature effects of the matrix flame to the ignition of UFAl particles under propellant conditions, the burning rates were measured of matrix samples with various fAP loadings of 20%, 40% and 50%, and with Al c/f ratio of 0/20 and 80/20. In addition, the burning rate results were compared to their propellant equivalent.

Figure 2(a) and Figure 2(b) show the burning rate as a function of pressure for matrix samples with fAP loading of 20% and 40% respectively, and with Al c/f ratio of 0/20 and 80/20, as well as its propellant equivalent. Figure 2(a) shows the burning rate of the matrix samples (fAP:20%) with Al c/f ratio of 0(30μm)/20(UFAl) and 80(30μm)/20(UFAl) were about the same. The addition of the 30μm Al in combination with the UFAl (Mix 30) seemed to have no significant effect on the matrix burning rates compared to those samples with only UFAl (Mix 27R). When comparing the matrix burning rates to its propellant equivalent (AP c/f 80/20 and Al c/f 80/20), the matrix samples showed on average a 30.5% reduction in rates, see Figure 2a. Figure 2b showed increasing the fAP loading to 40% for matrix samples with only 20% UFAl increased the burning rates by approximately 160% when compared to those equivalent matrix samples with only 20% fAP. Figure 2b showed that the presence of the 30μm Al in combination with the UFAl reduced the burning rate by ~12.8% compared to those matrix samples with only 20% UFAl. The burning rates of the matrix samples (Mix 28 & 31) were slightly lower compared to its propellant equivalent (Mix 25). Increasing the fine AP loading to 50% for matrix samples with only 20% UFAl increased the burning rates further by approximately 38% compared to its matrix equivalent with only 40% fAP loading, see Figure 2c. Figure 2c shows the burning rates of matrix samples with 20% UFAl were similar to its propellant equivalent with a slight deviation in rates at higher pressures.

Interpretation of Results

Section titled "Aluminum Ignition," discusses the reaction rate of Al particles being impeded by the presence of an oxide coating (Al_2O_3) that does not break down until the particle/agglomerate/droplet nears the melting temperature of the Al_2O_3 (2047°C). Traditionally, the temperatures needed to melt the Al_2O_3 in AP solid propellants were attained through the gas phase flame, which was composed of a complex AP-binder flame array. From the standpoint of Al ignition, the sites in the flamelet array that most affect propellant burning rate are those that are: (a) hot, (b) near the surface, and c) have both Al and oxidizer present.[2] Generally, the most critical flame needed to attain Al ignition/combustion close to the propellant surface is the LEF because of its approximate adiabatic flame temperature of 2300°C and its flame standoff distance of approximately 50μm. This allows the LEF to represent Al ignition sources capable of producing temperatures high enough to melt the Al oxide coating and inevitable initiating Al combustion.

Not all AP particles are capable of sustaining LEFs or even a diffusion flame. Earlier studies by Price et al[9,10] have shown that the existence of LEF is very dependent upon the size of the AP particle and pressure. From these studies, it was found that AP particle sizes of 10μm and smaller do not have LEFs below a pressure of 6.9MPa and are small enough to act as diluents for the binder fuel vapor. This results in faster mixing and establishes a binder-fine AP premixed flame referred to as a 'matrix flame'. This type of flame acts as a canopy flame across the propellant surface that has a considerably cooler flame temperature (~1100°C for conventional AP solid propellant) than LEFs.

From the foregoing, it is evident that the flamelet associated with the above matrix-based samples is the gas-phase flame associated with the matrix. The average flame temperature associated with the matrix flame prevents the melting of the Al_2O_3 oxide skin, and thus inhibits Al combustion. Preliminary combustion images and burning rate results from the matrix samples (see Figure 1 and Figure 2) show Al ignition and Al combustion (e.g., the luminosity of the ABR). The matrix samples with 20%, 40% and 50% fAP loadings had adiabatic flame temperatures (without the presence of Al) at 6.9MPa of ~1113°C, ~1511°C and ~1914°C respectively. Immediately, it is apparent the adiabatic flame temperatures associated with 20% and 40% fAP loading were low to melt the Al_2O_3 coating, while the adiabatic flame temperature associated with 50% fAP loading was ~1914°C at 6.9MPa. It is argumentative in the latter case whether the adiabatic flame temperature was approaching the threshold melting temperature of the Al_2O_3. Nevertheless, the results of the combustion images and the burning rate results of the matrix samples do show Al combustion with various degrees of ABR luminosity. These preliminary results may provide important clues to the ignition mechanism of UFAl particles.

Price[6] showed that during Al particle 'heat up', the oxide shell undergoes cracking that readily exposes the Al to the oxidizer species. Figure 3 shows typical expansion crack patterns in the Al oxide shell. These cracks are resealed by the oxidation of the Al at temperatures below the Al_2O_3 melting temperature; this is evident as small exothermic spikes in Differential Thermal Analysis (DTA) of regular Al.[11,12]

As the size of the Al particle is reduced (e.g., to UFAl ~ 0.1μm) the cracking of the Al oxide shell during heat up exposes the Al to the oxidizing species, as expected. However, in this particular case, the heat release from the Al oxidation represents a significant portion of the particles total volume compared to CSAl, see Figure 4. Instead of the cracks being resealed, the UFAl sized particle is forced into 'early ignition', thus the small exothermic peak seen in DTA data of regular Al is now replaced with one massive exothermic peak.[11,12] This may explain the sensitivity of ultra-fine Al particles to lower AP-binder flame temperatures.

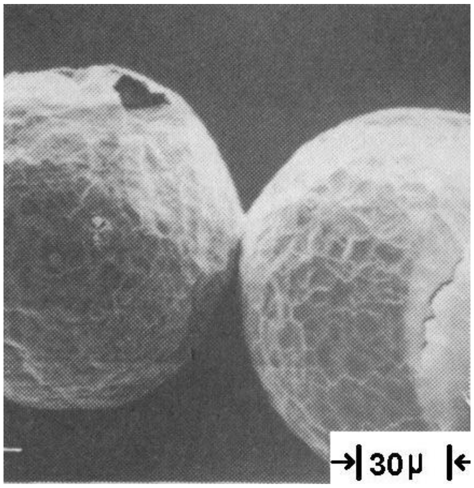


Figure 3:Cracked oxide shells of cooled Al particles that were heated to 1400°C on a sapphire plate in an oxygen-containing atmosphere. (Photo taken from Ref. 6-figure 3).

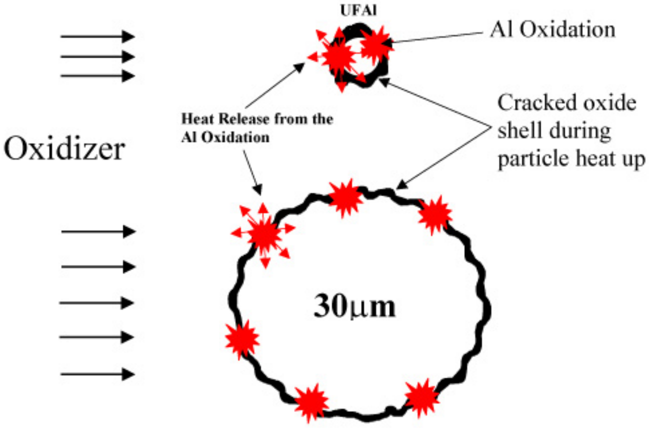


Figure 4: The heat release during Al oxidation with respect to the Al particle volume.

The availability of the oxidizer species may explain the variation in the ABR's luminosity (see Figure 1) and thus the burning rate results (see Figure 2). Ref 1-3 and 8 discusses the mechanistic importance of the Al combustion taking place closer to the propellant burning surface, with a corresponding large increase in burning rate due to the intense radiation field and elevated temperature near to the surface. The 10µm AP increases the availability of the oxidizer species for the Al by enhancing the diffusion i.e., reducing the diffusional distances between the oxidizer and the Al fuel. For Al to react 'effectively' not only must the oxide coating reach its melting point to expose the Al which is attained through appropriate Al ignition sites but there must also be sufficient availability of oxidizer diffusion to the Al. Reducing the total mass availability of oxidizer in the matrix sample reduces the total availability of the oxidizer species for the matrix flame (low O/F ratio) and the Al fuel. With 20% fAP, the matrix flame was hot enough to ignite the UFAl particles but limited by the oxidizer availability for Al combustion. This resulted in an overly fuel-rich ABR (see Figure 1a and Figure 1b), thus a reduction in ABR luminosity, hence lower burning rate compared to its propellant equivalent. The insensitivity of the matrix burning rates with the presence of the CSAl (30µm) in combination with UFAl (see Figure 2a) indicates that the contribution of CSAl to the combustion processes close to the propellant surface was limited. It may be significant that in an environment with limited availability of oxidizer (20% fAP or fAP/binder ratio of 56.35/43.65) that the UFAl's rapid depletion of oxidizer due to short diffusion time may have deprived the CSAl of any oxidizer. Increasing the fAP loading to 40%-50% increased the matrix flame temperature and more importantly, increased oxidizer availability for the Al fuel; thus increasing the luminosity of the ABR and hence aiding an effective Al combustion close to the propellant surface. As a result, the adiabatic flame temperature of the matrix flame at 6.9MPa with 20% UFAl (*with sufficient availability of oxidizer close to the propellant surface*) increases to ~2067°C and ~2352°C with 40% and 50% fAP respectively. This may explain the near equivalent matrix burning rates to its propellant equivalent. With 40% fAP, the increased availability of oxidizer no longer deprives the CSAl (30µm). In this particular matrix formulation, the reduction of the matrix burning rate of samples with blends of both CSAl and UFAl (see Figure 2b) may be due to the CSAl acting as a heat sink during it residence time on the propellant surface were it undergoes a complicated process of sintering and agglomeration.

Conclusion

The study represents a preliminary investigation into the ignition temperature of ultra-fine aluminum particles compared to conventional sized Al particles in AP-PBAN solid propellants. Matrix samples with 20% UFAl, and with various mass loadings of 10µm fAP, were used as a means to vary the AP-binder flame temperature. The fAP loading was chosen according to earlier studies[1,2,3,8] to determine the effects of using bimodal Al particle size distribution in AP solid propellant; one of the variables during the study was the AP c/f ratio. According to a preset family of formulations, the fAP loading was chosen as 20%, 40%, and 50% of the total 71% AP loading.

Preliminary results show UFAl sized particles ignite at lower gas-phase (oxidizer/binder) flame temperature than CSAl particles. The 'early' ignition of UFAl particles coupled with sufficient availability of oxidizer encourages the UFAl combustion to takes place closer to the propellant surface. It was argued that the precursor for early Al ignition was related to the particles oxide coating cracking during particle heat up and the heat release per unit volume (or per unit area) from Al oxidation. For UFAl, the heat release per Al particle volume during particle heat up was large enough to force particle ignition.

The contribution of CSAl particles in combination with UFAl generally showed an insensitivity to the matrix burning rates, re-enforcing earlier arguments[1-3,8] that the combustion of CSAl particles occurred further out from the propellant surface and made no significant contribution close to the propellant surface. The size of the CSAl may allow it to act as a heat sink during its complicated process of sintering-agglomeration during its limited residence time on the propellant surface. However, the early ignition of UFAl coupled with UFAl combustion close to the propellant surface may also induce early CSAl ignition because of the ABR's temperature field.

Acknowledgements

The experimental investigation was conducted by the authors at the Propellant Combustion Laboratory - School of Aerospace Engineering, Georgia Institute of Technology.

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