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Full Paper

Nano Aluminum Energetics: The Effect of Synthesis Method on Morphology and Combustion Performance

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Abstract

Nanoscale aluminum based energetic composites were prepared using polytetrafluoroethylene (PTFE) as an oxidizer, and optimized according to the maximum experimentally observed flame propagation rate in an instrumented burn tube. Optimization of the aluminum-based composites was performed using nanometric aluminum from two manufacturers, Argonide Corporation and Novacentrix, and the combustion results represent the first direct comparison of these two materials in a burn tube configuration. Argonide aluminum was found to consist of many fused spheres of nano aluminum mixed with some larger micron sized particles. Novacentrix aluminum consisted of spherical particles with a closer particle size distribution. The propagation rate optimized wt.-% aluminum powder values were 50 and 44.5 for Novacentrix and Argonide, respectively. At the optimized conditions, the time to steady propagation for both Argonide and Novacentrix were similar, however the startup time for the Novacentrix based mixtures was more sensitive to changes in the mixture ratio. The presence of micron sized aluminum and lower surface area, but higher active content in the Argonide mixtures resulted in lower propagation rates, pressurization rates and peak pressures but higher total impulse values. It was found that peak pressure is not the sole determining factor in propagation rate, but the highest pressurization rates correlate with propagation rate.

Keywords: Nanoenergetic, Aluminum, PTFE, ALEX, Nanothermite

1 Introduction

The use of nanomaterials in energetic compositions known as nanoenergetics has been widely documented by many researchers [1–7]. Dreizin [8] recently completed a review of metal-based reactive nanomaterials. The length scales of the particles employed (at least one dimension ≤ 100 nm) greatly increases the sensitivity, reactivity, heat release rate, and overall performance of equivalent compositions of larger particles. The widely accepted explanation for this behavior is the change from diffusion dominated processes to kinetically dominated processes, brought about by the small scales involved and intimate mixing of the materials.

The majority of research on nanoenergetics has focused on compositions that use aluminum as fuel. Typical oxidizers are those used in thermite reactions, such as MoO_3, CuO, Fe_2O_3, etc. [9–10], but the use of other oxidizers such as nitrates, iodates, or fluoropolymers are feasible as well [12–16].

Moore et al. [11] recently showed that certain combustion properties of Al/MoO_3 nanoenergetics can be duplicated in mixtures using larger particles, with the addition of only a small amount of nanomaterial. They showed that the ignition delay time for bimodal mixtures decreased drastically with the addition of 20 % or greater nano aluminum (n-Al). Combustion velocity was seen to increase constantly with n-Al addition, with a slight leveling off around 75 % n-Al.

PTFE has recently been used as an oxidizer in aluminum based nanoenergetic composites and tested in a burn tube configuration. Watson et al. [12] noted that using PTFE as an oxidizer resulted in lower flame speeds and higher peak pressures, indicating that a direct relationship between peak pressure and propagation rate does not exist. Yarrington et al. [13] found that the initial combustion behavior of Al/PTFE mixtures can change depending on the ignition method used.

The performance of many nanoenergetic formulations is now known, and more formulations continue to be discovered and characterized. The cost of the components is not typically discussed, but price is a factor in determining the applicability of nanoenergetic composites, as well as which nanoenergetic formulation will be used. Two aluminum manufacturers have been used by researchers

Table 1. Reported in this Table are the constituent material physical properties.

Material	% of active content	Nominal Size	Surface Area/$m^2\ g^{-1}$	Supplier
Novacentrix aluminium	79	80 nm	28	Novacentrix
ALEX aluminium	86	100 nm	12.7	Argonide Corp.
Zonyl® MP1150 PTFE Powder	100	200 nm	5–10	Dupont®

with the most frequency, Argonide Corp. and Novacentrix. Argonide aluminum is manufactured using the exploding wire process, and is commonly referred to as ALEX aluminum. Novacentrix aluminum is manufactured using the inert gas condensation method following plasma heating. With the widely varying material costs, it is important to know the cost and performance tradeoffs between different aluminum offerings.

The objective of this study is to analyze the performance of mixtures prepared using aluminum from two different manufacturers and compare the results. The diagnostic methods used for these comparisons and the results are presented in the following study.

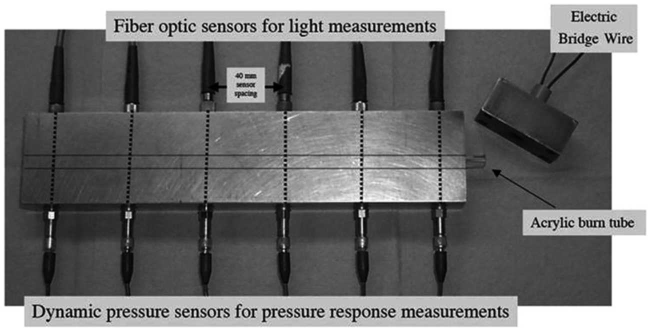

Figure 1. The instrumented burn tube setup, showing the locations of the pressure and optical fibers.

2 Experimental

2.1 Materials and Sample Preparation

The materials used in this study along with relevant properties are shown in Table 1. Aluminum particles are surrounded by an oxide passivation shell and the active content was measured by a volumetric method [14] and by thermogravimetric analysis (TGA). In the volumetric method a known amount of aluminum powder is placed into a flask containing a solution of NaOH in water which is connected to a manometer. The active aluminum in the particles reacts with the oxygen in the solution resulting in solid alumina and hydrogen gas products. The hydrogen gas pressure is measured with the manometer and the active content is calculated from the measurement. Active content is measured using TGA by oxidizing the aluminum powders in an oxygenårgon atmosphere at high temperatures and measuring the weight gain of the samples. The weight gain is directly related to the amount of active Al, and is assumed to come solely from aluminum conversion to alumina. To prevent premature aging of the sample materials, they are kept in an inert environment prior to nanoenergetic synthesis and testing. It is important to note the differences between the properties of different aluminum products. Although ALEX has higher active content, this ist likely due to the larger average particle size. Also, Novacentrix has a much higher specific surface area. The inverse proportionality between particle size and specific surface area is widely believed to contribute strongly to the increased reactivity of particles at the nanoscale.

Composites batches of 1 g each were prepared by combining fuel and oxidizer in a 20 mL glass vial and then sonicating the mixture in hexanes using a Branson Digital Sonifier 450 with a 6.35 mm diameter sonicating tip (type 102C). The mixtures were sonicated for 3 minutes at an output power of 200 W, a period of one second and a duty cycle of 60 %. The mixtures were then dried on a hot plate at 60 °C and sieved using a No. 60 standard mesh using and a stainless steel brush. The final result is a loose uniform powder.

2.2 Testing Apparatus

An instrumented quasi-1D burn tube was used in the characterization of the nanoenergetic composites. Bockmon [6] first used an instrumented burn tube for combustion characterization and the experiment was recently reviewed by Yarrington et al. [15]. The current experiments were performed using a much longer 24 cm long tube with six PCB Model 113A23 high frequency pressure sensors and six Thorlabs Model DET210 high speed photo detectors placed at 4.6 cm intervals (see Figure 1). The burn tubes were loaded at densities ranging from 17 % to 23 % of theoretical maximum density (TMD), depending on the mixture ratio. For a given mixture ratio, the maximum difference in packing density seen between mixtures using Alex and Novacentrix was 3 % TMD. Data was acquired using models NI-PCI-5105 and NI-PCI-6115 National Instruments DAQ boards. The materials were ignited by placing a small amount of Al/MoO_3 nanoenergetic in the top of the tube. A bare explosive bridge wire (Teledyne Risi Inc., #RP-1) was then discharged into the higher sensitivity Al/MoO_3 which, upon burning, ignited the nanoenergetic of interest. The smaller block shown in Figure 1 houses the bridge wire assembly and also provides confinement to the ignition end of the burn tube.

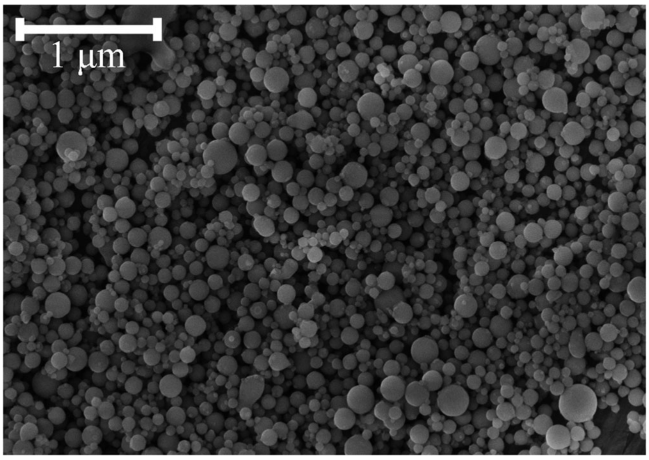

Figure 2. A SEM image of Novacentrix aluminum taken at 25 kX magnification.

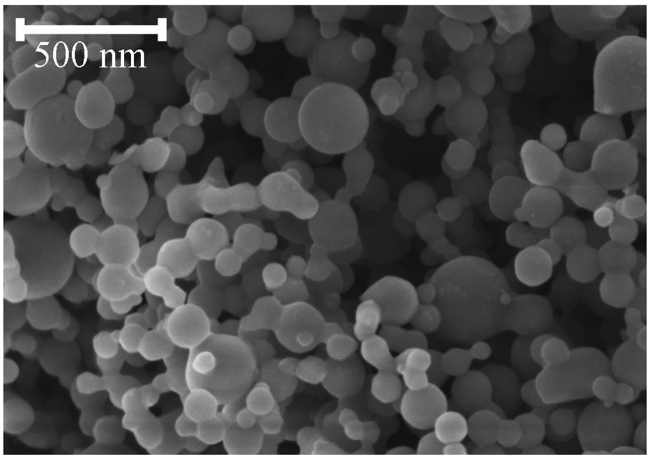

Figure 4. A 50kX magnification SEM image of ALEX aluminum.

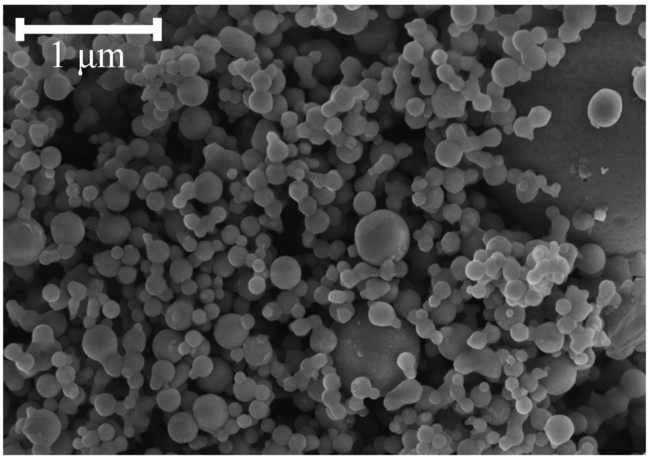

Figure 3. A SEM image of ALEX aluminum taken at 25 kX magnification.

3 Results and Discussion

Mixtures of PTFE and aluminum from both Argonide and Novacentrix were optimized to determine the mixture ratio which resulted in the highest propagation rate. As two different aluminum products were used in this study, a comparison of the two aluminum powders can be made both quantitatively and qualitatively. To the authors' knowledge, the direct comparison of the combustion properties of Argonide (ALEX) and Novacentrix n-Al composites in burn tubes has not yet been reported. The Argonide produced aluminum will be referred to hereafter as ALEX.

3.1 SEM Micrographs

Shown in Figure 2 and Figure 3 are SEMs of Novacentrix and ALEX n-Al, respectively. The difference between the two powders is readily seen. Novacentrix n-Al consists of nearly spherical particles (25–200 nm). Although the particles do tend to agglomerate, each particle is nevertheless a solitary sphere of oxide coated aluminum. In comparison to ALEX n-Al that is comprised of particles ranging in size from around 50 nm to larger than 1000 nm, the Novacentrix n-Al is relatively uniform. Figure 3 shows that in ALEX n-Al there are many nanoparticles, but there are also larger micron sized spheres of aluminum present in ALEX. These larger particles are the reason for the higher reported average particle size. The higher magnification image of ALEX (Figure 4) shows that the smaller particles are not all spherical. There are some spherical particles, but on the whole there are more particles that resemble fused spheres rather than solitary spherical particles. It is common to observe as many as ten aluminum spheres fused together. This reduces the available surface area of the individual spheres and can affect mixing as well. Due to the lower particle surface area of ALEX and the larger average particle size it is expected that ALEX will yield lower propagation rates, pressurization rates and longer ignition times.

3.2 Propagation Rate Optimization

The optimization process is relatively simple, and involves mixing several batches of material with different amounts of aluminum and PTFE, with fuel content varying by 5 wt.-%. The range of ratios tested was 35–55 wt.-% for Alex and 40–60 wt.-% for Novacentrix. Arrival times of the propagation front are measured as the initial rise in pressure and photodiode signal. The known distance between transducers and photodiodes and the time of arrival allows the propagation rate to be calculated. The propagation rate values at different mixture ratios were plotted and the optimized mixture ratio was calculated as the peak of a quadratic fit to the data points. The optimized composition was determined to be 50 and 44.5 wt.-% aluminum powder for Novacentrix and ALEX, respectively.

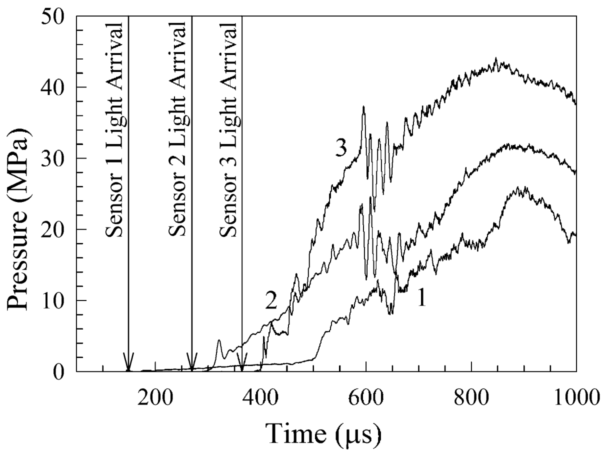

Figure 5. Pressure traces from the first three transducers for a 40/60 mixture of ALEX/PTFE.

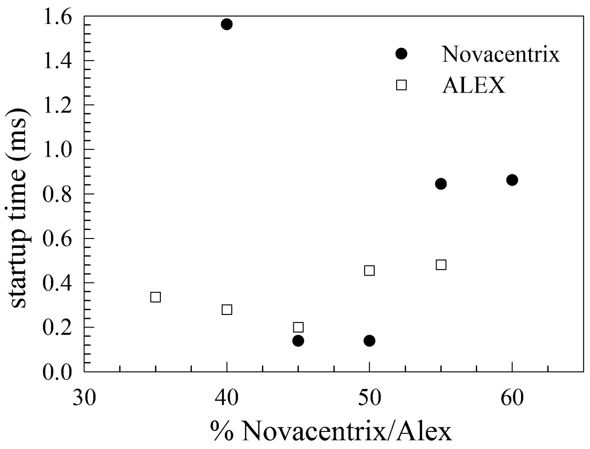

Figure 7. Times to high speed propagation for Al/PTFE composites.

3.3 Time to High Speed Propagation (Start-up Time)

An indication of the time needed to reach high speed propagation can be gained by analysis of the initial pressure traces. Figure 5 shows a typical pressure trace for the first three transducers. The fact that the pressure at the face of the first transducer in Figure 5 is initially constant is indicative of a deflagration mode present in the initial portion of the tube. By the time the propagation front reaches the second transducer a pressure wave has developed, indicated by the sharp initial pressure rise at 300 μs. The time of first light arrival is also indicated in Figure 5 for the first three transducer locations, and this shows that even though a reaction front has passed transducer one, the mode of reaction is still deflagration because the reaction front is not followed by a sharp pressure rise. Transducers two and three both show a sharp pressure rise approximately 40 μs after the detection of light. The presence of a pressure rise in transducer one at 500 μs is likely a pressure pulse that has propagated back through the tube. Due to the highly unsteady nature of the initial combustion just described, a useful metric to consider is a "start-up" time. This metric quantifies the amount of time taken to reach steady state including the ignition delay time.

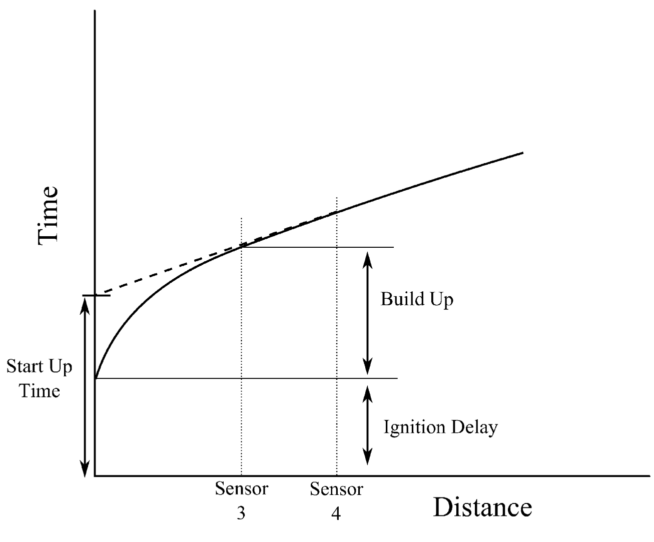

Figure 6. Conceptual diagram of the time to high speed propagation.

By using the propagation rate between two successive transducers in the steady state regime, an estimated time "zero" can be calculated. This time represents a theoretical time for the front to transverse a distance assuming no ignition delay and no transient behavior. The difference between this time and the actual time "zero" is an estimated "start-up" time. In reality, this time is a combination of two effects: 1) the ignition delay of the material and start of propagation by deflagration and 2) the time to pressure build up and start of convective deflagration. Figure 6 shows a diagram which outlines the concept of the start-up time. Even though this time is not a true "ignition" time, it is nevertheless useful in comparing the initial combustion behavior of different materials. This start-up time would be especially important in small devices where sufficient material is not available for full propagation to be achieved.

Figure 7 shows the start-up times for mixtures of Al/PTFE using both Novacentrix and ALEX aluminum. It is seen that for both Novacentrix and ALEX based mixtures, the shortest time was measured at approximately the optimized mixture ratio. This may indicate that at the optimized mixture ratio the ignition delay is shorter or the time to steady state is less. It is likely that the same processes (faster reaction rate and pressurization rate) that result in the fastest burning rate contribute to a shorter delay in reaching steady state and faster startup times. Surprisingly, it is also seen that using Novacentrix results in increased dependence on mixture ratio as seen by the increased startup times away from the optimized ratio.

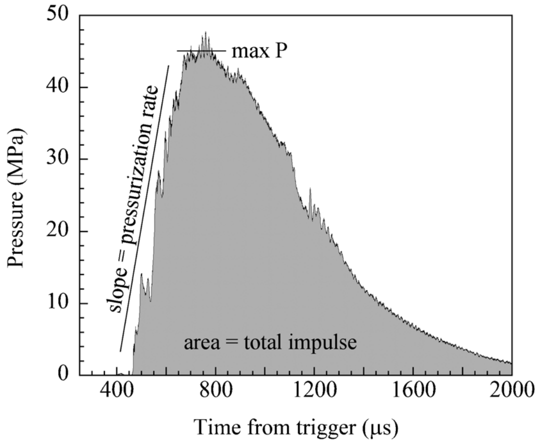

Figure 8. A representative pressure trace showing the various properties that can be calculated.

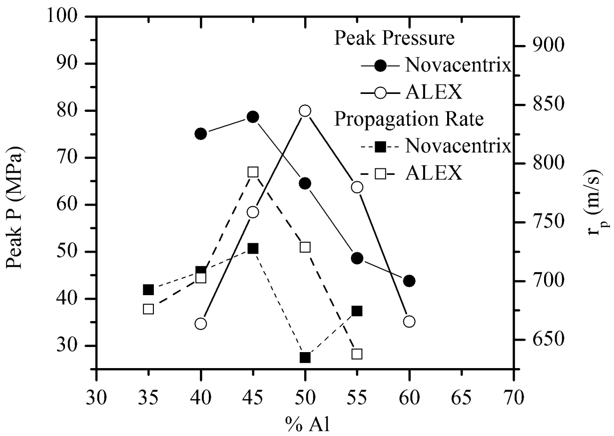

Figure 9. Influence of wt.-% aluminum on the peak pressure and flame propagation rates for ALEX and Novacentrix Al-PTFE composites.

3.4 Peak Pressure and Pressurization Rate

The data indicate that when considering the convective mode of burning, the pressurization rate as well as the peak pressure must be considered. It can be seen in Figure 5 and Figure 8 that the pressure in the burn tube is not constant, and a maximum pressure can be measured for each transducer. Figure 8 depicts the meaning of each of the three properties to be discussed in the following paragraphs and section: Peak pressure, pressurization rate, and total impulse.

Because transducer five reports the highest maximum pressure in almost all cases, the peak pressure reported in Figure 9 is that of transducer five. Moore et al. [11] and Yarrington et al. [15] have shown that peak pressure is not the sole determining factor for propagation rate in a confined burn tube, but in this study the two properties correlate for ALEX as seen in Figure 9 (r_p is the propagation rate).

Although the peak pressure at the optimized mixture ratio for Novacentrix n-Al was not the highest (see

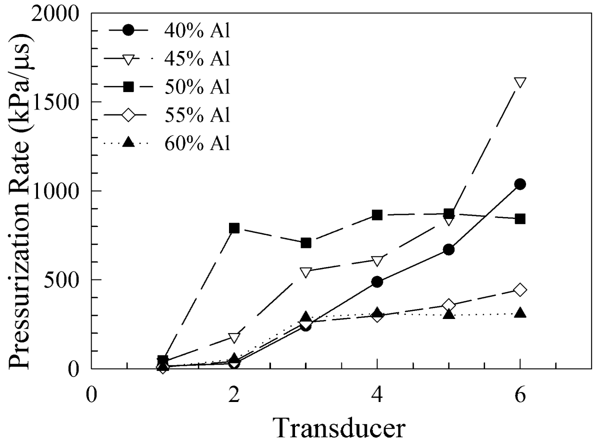

Figure 10. Pressurization rates at each transducer for Novacentrix Al/PTFE composites. The highest pressurization rates occur at the optimized mixture ratio.

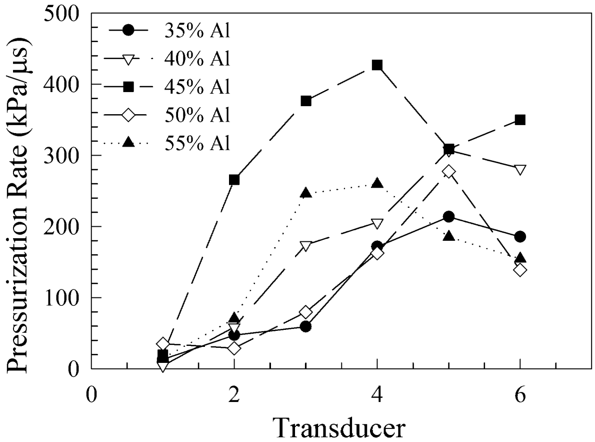

Figure 11. Pressurization rates at each transducer for ALEX Al/PTFE composites. The highest pressurization rates occur at the optimized mixture ratio.

Figure 9), it is seen in Figure 10 that at the optimized mixture ratio the pressurization rates for all transducers except the last were higher. The pressurization rate is calculated as the slope of the initial rise of the pressure trace. The highest pressurization rates for ALEX also correspond to the fastest burning rates. The pressurization rates for Novacentrix and ALEX based mixtures are shown in Figure 10 and Figure 11. This observation is significant because it could significantly reduce the time and material costs of screening mixtures. Rather than performing multiple burn tube experiments for optimization, smaller amounts can be tested and pressurization rates measured in a confined environment. This method of optimization is alluded to by the data, although it has not yet been tested in practice.

The pressurization rate trends are different as well, with pressurization rates increasing continually for Novacentrix based composites, and peaking at transducer four

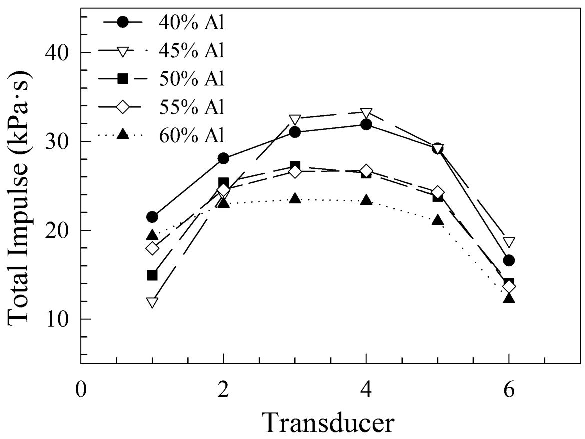

Figure 12. A plot of total impulse at each transducer and mixture ratio for Novacentrix Al/PTFE composites.

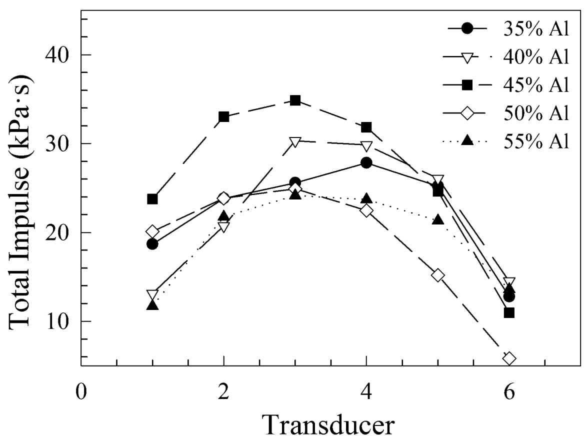

Figure 13. A plot of total impulse at each transducer and mixture ratio for ALEX Al/PTFE composites.

or five for ALEX based composites (Figure 10 and Figure 11). This ist likely due to the morphological differences between ALEX and Novacentrix aluminum. The larger particle size distribution of ALEX results in extended burning times as the large particles burn longer. At the end of the tube, the local driving pressure will not be as great after the propagation front exits the tube, and the pressure behind the wave is allowed to equalize. This is also seen in the pressurization rate values, which are much higher for Novacentrix aluminum based composites, reaching as high as 1600 kPa μs^{-1}, whereas the ALEX peak pressurization rate is significantly lower, 420 kPa μs^{-1}.

3.5 Total Impulse

Data analysis revealed that the peak total impulse values were higher for ALEX n-Al. The total impulse is a combustion characteristic that serves as a means of comparing the effect of pressure over time. The total impulse is useful as a comparative metric and is calculated as the integral of the pressure trace (product of pressure and time) with units of kPa μs^{-1}. The pressure trace from each transducer can be integrated and the results from this analysis are shown in Figure 12 and Figure 13. Although the values for ALEX and Novacentrix do not differ significantly, the result is significant. When a sustained force over a longer time is desired ALEX aluminum may be the desirable choice when all factors, including material cost, are considered. This result can be explained both by the morphology and active content of the different powders. Both the larger particles and the higher active content will result in longer burning times for ALEX, allowing for similar performance to Novacentrix in total impulse. End effects cause the total impulse of transducers five and six to be lower than transducer four in all cases. However, in the faster mixtures (45%/50% ALEX, 45%/50% Novacentrix), total impulse from transducer four is seen to be lower than transducer three. The decrease in total impulse is due to the changing conditions in the tube (and at the transducer face) resultant from the combustion front exiting the end of the tube. At this point, a constant volume assumption is no longer valid, and a pressure wave will propagate back through the tube allowing the transmission of pressure information. A faster burning rate will result in an earlier time of arrival of this event, which is manifest in the total impulse trends.

4 Conclusions

Al/PTFE nanoenergetic composites using two different aluminum types were characterized in instrumented burn tubes, a comparison that had not been performed previously. The presence of µm-sized aluminum particles in ALEX aluminum indicated that the combustion characteristics would likely differ. The burning rates optimized at 50 and 44.5 wt.-% aluminum for Novacentrix and ALEX, respectively. Startup times for both composites were shortest at the optimized mixture ratio, and the startup times for Novacentrix aluminum were seen to be very sensitive to changes in the mixture ratio. It was also seen that the highest pressurization rates for both composites occurred at the propagation rate optimized mixture ratio, in contrast to the peak pressure that showed weak correlation with the propagation rate. This observation has potential benefits for screening potential mixtures or in optimization procedures. It may be possible to use only a small amount of material for testing, and measure pressurization rates in a confined environment as opposed to performing multiple burn tubes. Total impulse was calculated for each transducer, and was slightly higher for ALEX aluminum even though the burning rates for Novacentrix aluminum were higher, a significant finding considering the varying costs of the materials. Also, because ALEX shows higher total impulse, it will perform better in applications where a sustained pressure over time is desired.

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