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# **Preparation and Characterization of Aqueous** Nanothermite Inks for Direct Deposition on SCB Initiators

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Abstract: Nanothermites are a promising replacement energetic for many devices but their use has been limited by high sensitivity during processing, hazardous processing solvents, and time consuming deposition. Incorporating processing and deposition into a single step, especially if no organic solvents were used, could allow nanothermites to be applied safely in a wider range of applications. This work reports on the performance and characterization of direct-deposited water processed nanothermite inks on semiconductor bridge (SCB) initiators. Specifically, it investigates the replacement of nanothermites processed by resonant mixing (Resodyn LabRAM) in the solvent N,N-dimethylformamide (DMF) with nanothermites processed in water. Processing safety and mixture performance were then characterized. It was found that water processed nanothermites were stable for up to 480 min in a water

bath at 50 °C only if both metal and metal oxide particles were coated with palmitic acid. In addition, water processed nanothermites were found to have better mixing intimacy, which resulted in better performance than nanothermite processed in DMF. Direct deposition of water processed nanothermites also mitigates electrostatic discharge (ESD) sensitivity, while the material remains wetted, improving processing safety dramatically. For the system investigated, it was found that processing at a solids loading of 30 vol.% resulted in a high density, high performance ink that was deposited directly onto the SCBs. This resulted in a 25% reduction in the all fire threshold over traditional energetics. This mixing approach uses an environmentally friendly mixing medium, can result in a higher density final material, and allows safe one-step mixing and deposition.

**Keywords:** Resonant mixing · Nanoenergetics · High viscosity mixing · Water processing · SCBs

### 1 Introduction

Igniters and initiators have widespread use in both military and civil applications stretching from explosive detonation trains to firearm propellants and airbag inflation systems [1-3]. Primary explosives such as lead azide currently play a crucial role in many explosive initiation systems but pose significant health and environmental issues in addition to being highly sensitive [4]. There is a need for safer, more environmentally friendly replacements for such energetics.

Current nanothermite research has achieved ignition performance similar to that of lead azides and primary explosives in some applications [5]. The nanoscale particles in a nanothermite have high interfacial surface areas, which increases the kinetic transport rate, thereby increasing the burning rate by several orders of magnitude [6]. Properly processed, nanothermites provide enough energy to be used in a variety of energetic material applications while forming more benign reaction products (e.g. lead free). Previous work by Tappan et al. [7,8] investigated the use of nanothermites on semiconductor bridge (SCB) initiators as a means to integrate energetic processing with the production of SCB initiators themselves. Despite promising characteristics, including ignitability and a small extinction diameter, the most widely used processing methods have significant safety hazards, including electrostatic discharge (ESD)

sensitivity and the use of organic solvents in large quanti-

To eliminate hazardous solvents, water has been proposed as an alternative mixing medium. This has been shown to decrease the sensitivity of the nanoscale energetic mixtures during processing [10]. However, nano-sized aluminum (nAI) particles can degrade rapidly when exposed to water [11,12], decreasing performance and introducing the potential for thermal runaway during processing. To overcome this, the addition of a surface modifier, ammonium dihydrogen phosphate (ADP), has been used to inhibit the continued reaction between water and nAl [13]. However, there is still some evidence of degradation during

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initial mixing [10, 11, 14, 15]. Particle coatings such as organic acids (e.g. oleic and palmitic acid) have also been considered to reduce the degradation of nAl when exposed to water and to improve aging characteristics. For example, previous work by Puszynski et al. [11] has shown that coating nAl particles with hydrophobic oleic acid can reduce the reaction rate of nAl with water. The use of these coated particles could allow for water processing without any initial degradation of nanoaluminum, but may introduce new issues including poor dispersion of particles during mixing due to the hydrophobic coating.

The objective of this work was to more fully investigate the safety of high solids loading resonant mixed water processed nanothermites, assess their performance against a nanothermite processed via resonant mixing in DMF, and demonstrate direct-deposition onto SCB initiators.

### 2 Experimental

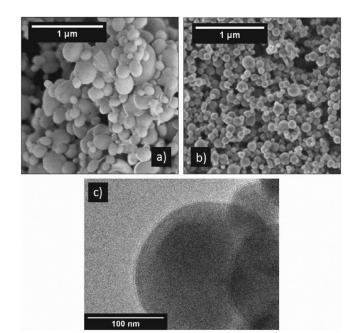
#### 2.1 Processing

Three separate processing methods were used to prepare the  $Al/Bi_2O_3$  thermite system. These are as follows: (1) DMF/FC-2175, a system in which reactant particles pre-coated with the fluoropolymer FC-2175 are combined via resonant mixing in dimethylformamide, (2) Water/ADP, a system in which non-coated reactants are combined via resonant mixing in water/ADP (a reaction inhibitor), and (3) Water/PA-L-ALEX, a system in which palmitic acid coated aluminum (L-ALEX) is combined with  $Bi_2O_3$  via resonant mixing in water with dispersant. In addition to these three formulations, several other systems were studied to assist in understanding stability in water; namely the metal Ni and the metal oxides  $Fe_2O_3$  and  $Bi_2O_3$ . A detailed description of the methodologies used follows.

The DMF/FC-2175 thermite was prepared with  $Bi_2O_3$  (Sigma Aldrich, 90–210 nm) and nAl (Novacentrix, 80 nm; 77% active aluminum) [16], and was de-sensitized with 5 wt.-% FC-2175 (Mach 1 lnc.) binder to reduce handling sensitivity and to improve adhesion to the bridge surface. SEM images of the particles used in this study are shown in Figure 1.

The FC-2175 binder was crashed onto the bismuth oxide and nAl particles separately prior to mixing [17]. In this process constituents were combined at a ratio of 130.7 mg nAl/16.8 mg FC-2175 and 869.3 mg  $\rm Bi_2O_3/35.9$  mg FC-2175 in acetone (5 mL) and were sonicated for 90 s using a sonicating horn (Branson Digital Sonifier 450, model 120C) at 50% intensity at a duty cycle of 80% (0.8 s ON, 0.2 s OFF). After 60 s of mixing, hexane (40 mL, Macron Chemicals, 60% n-hexane) was added to precipitate FC-2175 out of solution. After mixing, coated particles were poured out into a metal pan and allowed to dry for 48 h in air.

After drying,  $Bi_2O_3/FC-2175$  (905.2 mg) and nAI/FC-2175 (130.7 mg) were combined inside a 10 mL slip-tip plastic syringe (BD, Franklin Lakes, NJ), and *N,N*-dimethylformamide



**Figure 1.** SEM images of (a) 90-210 nm Sigma Aldrich  $\text{Bi}_2\text{O}_3$ , (b) 80 nm Novacentrix nAl, and TEM of (c) 100 nm palmitic acid-coated L-ALEX nAl from Argonide Corporation (shown to illustrate coating thickness).

(DMF) (Sigma Aldrich, anhydrous, 99.8%) was added to achieve 30 vol.% solids loading (0.332 mL).

Inhibited aluminum-bismuth(III) oxide (Al/Bi<sub>2</sub>O<sub>3</sub>) nanothermites (water/ADP) were prepared with Bi<sub>2</sub>O<sub>3</sub> (869.3 mg, Sigma Aldrich, 90–210 nm) and nAl (130.7 mg, Novacentrix, 80 nm; 77% active aluminum) inside a 10 mL slip-tip plastic syringe. A 30 vol.% solids loading was achieved by adding water/ammonium dihydrogen phosphate (0.332 mL, ADP) solution. This solution had been previously prepared with 3 or 7 wt.-% (with respect to aluminum) ADP (Sigma Aldrich). Inhibitor quantities were chosen based on common levels used by Puszynski et al. [11] and Kittell et al. [15].

For nanothermites prepared with coated nAl (water/PAL-ALEX),  $\mathrm{Bi}_2\mathrm{O}_3$  (883.1 mg, Sigma Aldrich, 90–210 nm) and L-ALEX nAl (116.8 mg, Argonide Corporation, palmitic acid coated, 50 nm, 87.5% active aluminum) were combined with 3 wt.-% dispersant (BYK, Disperbyk 192) relative to nAl inside a 10 mL slip-tip plastic syringe and water was added to achieve 30 vol.% solids loading (0.329 mL).

All syringes were set such that 1 mL of free volume remained. Individual syringes were then sealed with a strip of Airtech Flashbreaker 1 tape, inserted into an in-house polytetrafluoroethylene (PTFE) fixture [18], clamped in a LabRAM resonant mixer (Resodyn Acoustic Mixers, Inc., Butte, MT) and mixed at 80% intensity (approx. 95 g). Each mix cycle consisted of two 8 min sessions with a wait period of 1 min between sessions during which the syringe was inverted.

Dry powders for Parr cell experiments, scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS),

and electrostatic discharge (ESD) sensitivity testing were obtained by brushing dried mixtures through a #40 sieves (425  $\mu m)$  to break up agglomerates. Extreme sensitivity of dried nanothermites required mixtures to be brushed through in 20–30 mg increments to mitigate dangers presented by inadvertent reaction of material. Direct deposition of formulations onto semiconductor bridges (SCB's) was conducted with wetted nanothermites immediately following mixing.

Additional materials and powders used for stability verification included iron(III) oxide [44  $\mu$ m (-325 mesh), Firefox Enterprises], nano-sized nickel (0.08-0.15  $\mu$ m, Alfa Aesar), nanoscale alumina (80 nm, 99.5% purity, US Research Nanomaterials, Houston, TX), and buffer solutions with pH values of 4.01 (product no. 2500), 7.00 (product no. 2520), and 10.00 (product no. 2540) (EK Industries). These materials were used to assist in understanding the stability of nAl in water when combined with various constituents. This was done by adding individual constituents (e.g. Ni, Fe<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, or organic acid coated Bi<sub>2</sub>O<sub>3</sub>) to a dilute water solution and measuring the solution pH with time.

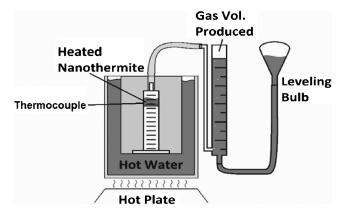
#### 2.2 Analysis and Instrumentation

Temperature rise during mixing was measured in-situ using K-type thermocouples (5SRTC-KK-K-30–36, Omega Engineering Inc.). Inert compositions of each nanothermite were prepared by replacing bismuth oxide with nanoscale alumina. For 1 g batches, preparation was accomplished as described above. To quantize the increase in mixture heating caused by scaling batch size, 20 g batches were also prepared. These batches were processed using the same resonant mixing profiles described previously, but used a larger 30 mL polypropylene container (McMaster-Carr, Part No. 42905T22). The thermocouple was inserted into both containers such that the thermocouple tip lay beneath the solvent level of the mixture and the container remained sealed.

Stability at elevated temperature for mixed nanothermites was determined by submerging loaded mixing containers in a 500 mL water bath maintained at 50 °C. Gas evolution was measured using a 50 mL graduated burette and levelling bulb, while thermal rise was measured by a K-type thermocouple inserted into the fixture such that it contacted the edge of the syringe body at the location of the nanothermite. A diagram of the experimental setup is shown in Figure 2.

The effects of the addition of a metal oxide to water was determined by adding adequate metal oxide to achieve 0.4% volumetric solids loading in water (10 mL). The pH of this water/metal oxide solution was measured by a PHE-3700 probe connected to a PHH-37 pH meter while being stirred with a magnetic stir bar.

Ignition and combustion properties were characterized in a closed Parr cell. Unconfined nanothermite powder  $(50\pm0.05 \text{ mg})$  was spark ignited in air at one atmosphere



**Figure 2.** Diagram of experimental setup for elevated temperature stability.

and room temperature in a 71.2 mL stainless steel Parr cell. A 113B27 PCB Piezotronics pressure transducer with a sensitivity of 7.25 mV kPa<sup>-1</sup> measuring the internal pressure of the Parr cell was used to determine pressurization rates and ignition delay. The transducer signal was passed through a PCB Piezotronics model 482A22 ICP signal conditioner and was recorded on a Tectronix 4034 digital phosphor oscilloscope with a sampling rate of 250 MS/s. Pressurization rate was calculated at the inflection point with the steepest slope of a sixth order polynomial fitted to the initial pressure rise. The ignition delay was defined as the time elapsed from piezoelectric spark discharge until the time at which the pressure increased above the average steady state pressure level for 4 µs (1000 samples), which was found to adequately indicate a signal above the noise level.

The ESD sensitivity tests were conducted on  $10\pm0.05\,\mathrm{mg}$  samples of semi-confined nanothermite powder centered on an aluminum pan and circled by a PTFE washer. The powder was tested in air at a relative humidity between 20% and 40% as defined by MIL-STD-1751 [19]. A "Go" condition was defined as any audible or visual reaction. The testing apparatus used was an adjustable voltage, approaching electrode device with oscillating spark discharge [20].

Energy dispersive spectroscopy (EDS) characterization of mixing quality was conducted with a JEOL7000F field emitting scanning electron microscope (FESEM) with an Oxford Microanalysis System X-ray detector operating at 20 keV with a working distance of 10 mm at 200×magnification. SEM/EDS analysis was conducted on four reactive mixtures to help interpret the trends observed in Parr cell experiments. These included a nanothermite resonant mixed in DMF and both inhibited and coated nanothermites resonant mixed in water all at 30 vol.% solids loading.

Semiconductor bridge (SCB) ignition threshold was determined using SenTest probability software with a linear Neyer D-optimal test design [21]. For each mixture, a set of twenty  $84 \times 42 \,\mu\text{m}$  90B2 SCB bridge initiators supplied by

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Ensign-Bickford Aerospace and Defense (EBA&D) (Simsbury, CT) was wet loaded with approximately 30 mg of nanothermite (dry). Each SCB then had a 150 mg booster charge of titanium sub-hydride potassium perchlorate (THPP) pressed in at 1.0 GPa ( $1.5\times10^5$  psi) in two 75 mg increments. Articles were placed into an in-house PTFE fixture and connected to a L10074 capacitive discharge SCB fireset from EBA&D (capacitance of 2.02  $\mu$ F) powered by a variable voltage power supply at voltages between 3 and 15 V (model 1692, BK Precision, Yorba Linda, CA). A "Go" condition was defined as any audible or visual reaction.

**Supporting Information** (see footnote on the first page of this article): Electrostatic Discharge Sensitivity of Dry Nanothermite Mixtures; Color image of Figure 8.

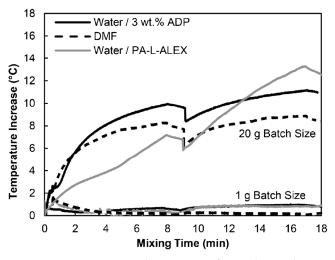
### 3 Results and Discussion

### 3.1 Stability and Safety

Resonant mixing relies on a high number of particle-particle collisions to evenly distribute constituents. These collisions can cause rapid heating of the mixture, which could present a danger at larger batch sizes, especially if instability at elevated temperature leads to thermal runaway. It is crucial that systems be stable at elevated temperatures before scaling is attempted.

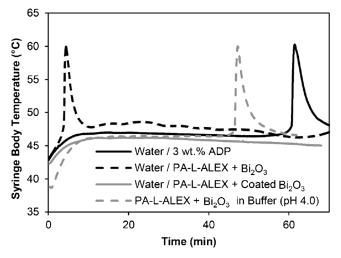
Previous work has shown that while ADP inhibited nAl/ water mixtures may be stable at room temperature, prolonged exposure to elevated temperatures results in degradation of the nAl [11,22,23]. Therefore, the thermal rise during mixing was measured to determine the relative safety of processing for small batches and to illustrate the dangers posed by scaling. To accomplish this a mock nanothermite in which Bi<sub>2</sub>O<sub>3</sub> was replaced with a proportional volume of 80 nm alumina was used. Both 1 g and 20 g batches were considered. As shown in Figure 3, 1 g batches of both water processed mock nanothermites resulted in about 1°C thermal rise after 16 min of mixing, only slightly more than was observed when DMF was used as the mixing medium. However, when the batch size was scaled to 20 g, the thermal rise in all mixtures considered increased significantly. For systems inhibited with 3 wt.-% ADP an 11 °C thermal rise was observed, whereas for the system processed with DMF/FC-2175 the thermal rise was only 9°C. Both ADP inhibited and DMF/FC-2175 systems follow similar heating trends, indicating that particle-particle friction is primarily responsible for the observed heating. However, when coated nAl was used a thermal rise of 13°C occurred during the mixing cycle and a linear heating trend was observed indicating potential heat generation. It is clear from these results that elevated temperatures resulting from mixing is a critical consideration for safely scaling and preparing nanothermites mixtures.

While some research has investigated the stability of dilute, inhibited water/nAl systems [8,24], systems processed at higher solids loadings have yet to be fully as-



**Figure 3.** Temperature rise during mixing for mock nanothermite systems processed with water/ADP, water/PA-L-ALEX, and DMF for 1 g and 20 g batch sizes. Mixing was paused in each experiment between minutes 8 and 9, while the syringe was inverted.

sessed. In the case, where nAl is used in conjunction with additives or oxides, it is especially important to determine the stability of the combined system. In this work it was found that nanothermites processed with water/ADP and water/PA-L-ALEX both resulted in rapid gas evolution and self-heating after an extended temperature excursion of 50 °C (Figure 4). It was observed that gas generation coincided with the onset of thermal rise, indicating reaction of nAl and water, creating hydrogen gas. Although this production occurred earlier for the water/PA-L-ALEX mixtures, the reaction did not appear to proceed to as great of an extent, producing 31 mL of gas after 70 min as compared



**Figure 4.** Syringe body temperature for inhibited, L-ALEX coated nAI, buffered L-ALEX coated nAI, and L-ALEX coated nAL/nBi $_2$ O $_3$  water processed nanothermites as a function of immersion time in a heated bath.

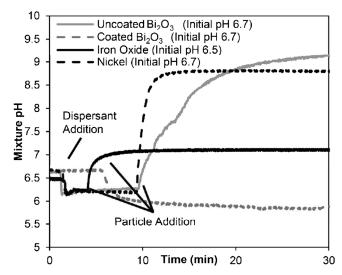
to 44 mL gas with the inhibited 3 wt.-% ADP mixture. In both cases, heating at atmospheric pressure in an unconfined system produced over 30 mL of gas from approx. 1 mL initial volume. In a confined system with more mass, pressurization could result in bulk ignition of the energetic. Systems with 3 wt.-% ADP present to inhibit the nAl reaction (water/ADP) were observed to be thermally stable for approximately 60 min under these conditions, although some slow production of gas was observed beginning at 10 min. Self-heating and gas evolution in water/PA-L-ALEX was observed after only 6.5 min, with gas production coinciding with the thermal excursion. This was surprising considering the extended stability of neat coated nAl under similar conditions (over 800 min). This illustrates the effect of other constituents on the degradation of coated nAl.

It was initially hypothesized that during resonant mixing hard oxide particles sheared the hydrophobic coating from nAl particles. However, the replacement of Bi<sub>2</sub>O<sub>3</sub> particles with harder alumina particles of comparable size (Moh's hardness of 4.5 vs. 9.0) failed to reproduce rapid heating and instead behaved similarly to the neat coated nAl. To further explore this, Bi<sub>2</sub>O<sub>3</sub> was replaced with nano-sized nickel (Ni) to better match the density of bismuth oxide. This mixture was observed to also heat similarly to the base material for both Resodyn mixed and hand mixed systems indicating that shearing of the surface layer was not a major factor in the observed heating.

Previous work by Kittell et al. [15] showed that palmitic acid coated nAl was stable in slightly acidic solutions, but became less stable in basic conditions. In this work it was observed that reducing the initial pH of the solution through the addition of a buffer resulted in a lower final pH after oxide addition than unbuffered solutions. This led to the hypothesis that the addition of nickel or an oxide increases the solution pH, driving the degradation reaction. It was observed that the addition of Ni, Bi<sub>2</sub>O<sub>3</sub>, or Fe<sub>2</sub>O<sub>3</sub> to a solution of water and dispersant (dilute mixtures) caused a rapid increase in mixture pH (Figure 5), which may contribute to the self-heating of nanothermites with coated nAl at elevated temperatures. This rise in pH is likely due to slight interaction of Bi<sub>2</sub>O<sub>3</sub> in the acidic solution.

Experiments with live nanothermites confirmed that lower solution pH improves stability at elevated temperatures. It was observed that for PA-L-ALEX nanothermite mixtures processed in an aqueous buffer solution with an initial pH of 4.0 were stable at elevated temperatures for significantly longer than mixtures in water (47 min versus 6.5 min) (Figure 4). Most importantly, it was also shown that the instability of coated L-ALEX particles when mixed in water with Bi<sub>2</sub>O<sub>3</sub> can be mitigated by coating *both* nAl and nBi<sub>2</sub>O<sub>3</sub> particles in organic acids (Figure 5). When a hydrophobic acid coating was used on both particles the stability in a heated bath at 50 °C was extended to over 480 min before gas production was observed.

Post-processing of nanothermites is also of importance with regards to application in devices. In dry powder form



**Figure 5.** Mixture pH of water/metal and water/metal oxide systems as a function of time.

**Table 1.** Electrostatic discharge sensitivity of dry nanothermite mixtures.

Ignition Energy	Reactive mixture			
	3 wt% ADP	7 wt% ADP	L-ALEX	DMF/FC-2175
0.1 μJ	0/5	0/5	0/5	0/5
لـ 1.0 μJ	2/5	4/5	0/5	0/5
10 μJ	5/5	3/5	3/5	0/5
لبا 100	5/5	4/5	3/5	0/3
1 mJ	-	-	-	2/2

nanothermites are known to be very sensitive to ESD [9,13]. Sensitivity testing for ESD was conducted on each mixture to determine its relative safety for handling (Table 1). In the dry state, all water processed nanothermites were so sensitive to ESD that the apparatus available did not have sufficient resolution to give statistically valid results. For these sensitive mixtures, the number of ignitions out of five is reported at several energy discharge levels.

In ESD sensitivity testing, water/ADP systems were observed to be the most sensitive, with no-fire thresholds below 1  $\mu J$ , and Water/PA-L-ALEX nanothermites being similarly sensitive with a no fire threshold below 10  $\mu J$ . For the nanothermite processed with DMF/FC-2175 a significantly higher no-fire threshold, on the order of 100  $\mu J$ , was observed due to the 5 wt.-% binder that also acts as a desensitizer. It should be noted that at these sensitivity levels, ESD cannot be effectively mitigated, making processing of dry nanothermite powders extremely hazardous. However, it has been shown that wetted nanothermites are much less sensitive to ESD [25]. Specifically, both coated nAl and inhibited nAl water processed systems were insensitive to ESD (no-fire thresholds above 250 mJ) when tested immediately after wet deposition at 30 vol.% solids.

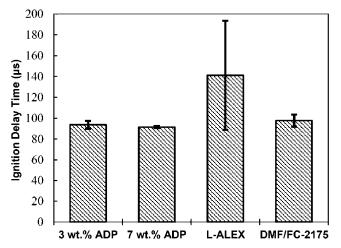
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### 3.2 Mixing Quality

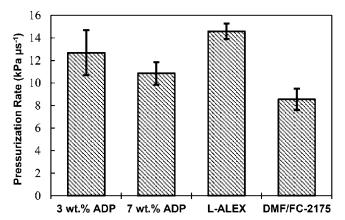
Parr cell ignition delay time is generally influenced by the intimacy of mixing of a nanothermite. Intimately mixed systems will have a shorter diffusion distance between particles, resulting in faster propagation through the particle bed and an earlier pressure rise following ignition. As shown in Figure 6, water/ADP inhibited nanothermites were observed to have ignition delay times comparable to the DMF/FC2175 system (93.7  $\pm$  3.8  $\mu$ s for 3 wt.-% ADP,  $91.6\pm1.1~\mu s$  for 7 wt.-% ADP, and  $97.7\pm5.8~\mu s$  for DMF/FC-2175), indicating similar mixing quality. Nanothermites with coated nAI (water/PA-L-ALEX) were observed to have much longer average ignition delay times and larger variation than other mixtures (141.2 $\pm$ 52.3  $\mu$ s). While in previous studies with DMF-processed nanothermites [18] the ignition delay time and ignition delay time variance was attributed to particle intimacy and mean agglomerate size, in this case the increase in ignition delay time and variance is likely related to ignition and propagation inconsistencies tied to the additional palmitic acid coating present.

It can be inferred from previous work by Perry et al. [26] that pressurization in a Parr cell is directly related to the burning rate of a given material. For nanothermites, a more intimately mixed energetic will have higher pressurization rates due to a shorter diffusion distance between reactants and more interfacial contact areas, both of which increase the burning rate.

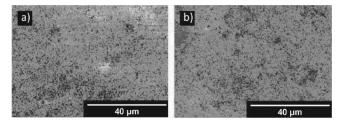
The water/PA-L-ALEX nanothermite was observed to have the highest pressurization rate  $(14.6\pm0.7~{\rm KPa\,\mu s^{-1}})$ , which typically corresponds to the most intimate mixture of reactants of the systems assessed (Figure 7). However, the gas contribution from combustion of the coating may also play a role. Both inhibited nanothermites had higher measured pressurization rates than the DMF/FC-2175 system  $(12.7\pm2.0~{\rm kPa\,\mu s^{-1}}$  for 3 wt.-% ADP,  $10.9\pm$ 



**Figure 6.** Parr cell ignition delay time for water processed and DMF/FC-2175 nanothermites.



**Figure 7.** Parr cell pressurization rate for water processed and DMF/FC-2175 processed nanothermites.



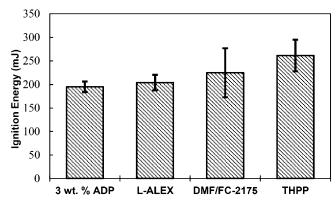
**Figure 8.** SEM/EDS of water/PA-L-ALEX (left, a) and DMF/FC-2175 processed nanothermite (right, b). Red=Al, green=Bi, blue=O. Color images available as Supporting Information (Figure S1).

1.0 kPa  $\mu s^{-1}$  for 7 wt.-% ADP, 8.6  $\pm$  1.0 kPa  $\mu s^{-1}$  for the DMF/FC-2175), indicating intimate mixing of constituents.

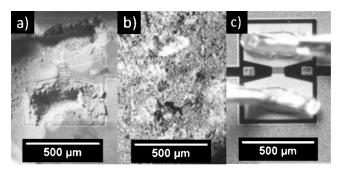
In analysis of SEM/EDS images (Figure 8), the water/PA-L-ALEX nanothermite was observed to generally have more uniform dispersion of particles along with a smaller mean agglomerate size near 4  $\mu m$  as compared to the DMF/FC-2175 processed nanothermite, which contained several areas of elevated aluminum concentration on the order of 15  $\mu m$  or larger. Improved dispersion is likely due to the use of an effective dispersant, and confirms the trends observed in the Parr cell pressurization rates. This indicates that, as predicted, the large variation in Parr cell ignition delay is not caused by large mean agglomerate size but by the organic surface coating on the aluminum particles themselves.

### 3.3 SCB Performance Characterization

The semiconductor bridge initiation threshold is a measure of ignition sensitivity and presents an application to which nanothermites are particularly well suited. SCBs typically function by vaporizing the narrow doped silicon bridge with a short pulse of high current and can form a plasma cloud in the region directly above the bridge [27]. This plasma cloud ignites the output mixture of the device. As bridge size decreases, the size of the plasma cloud decreas-



**Figure 9.** Ignition energy threshold for water and DMF/FC-2175 processed nanothermites, and traditional energetic formulation THPP. Error bars represent 0.999 and 0.001 probability of firing.



**Figure 10.** Examples of (a) bridge surface conformity for DMF/FC-2175 nanothermite, (b) bridge surface conformity for THPP, and (c) bridge features for comparison.

es and the conformity of energetic materials to the bridge becomes of greater importance.

In this study all nanothermites had initiation thresholds lower than titanium sub-hydride potassium perchlorate (THPP) (195.0 µJ for 3 wt.-% ADP, 204.0 µJ for water/PA-L-ALEX, 224.7 μJ for DMF/FC-2175, 261.4 μJ for THPP), a commonly used energetic in SCBs as shown in Figure 9. This is likely due to better conformity of the energetic to the bridge. Specifically, well dispersed nanoscale particles will coat the bridge more uniformly than um sized particles that can be on the same order of size as the bridge. Both water processed nanothermites were observed to have a smaller threshold spread, the energy difference between all-fire and no-fire thresholds, than either DMF/FC-2175 processed nanothermite or THPP systems (22.4 µJ for 3 wt.-% ADP and 47.4 µJ for water/PA-L-ALEX vs. 103.4 µJ for DMF/ FC-2175 and 66.8 µJ for THPP). This is due to the ink-like consistency of water processed nanothermites that allows the material to flow around the bridge resulting in more consistent contact (Figure 10).

### 4 Conclusions

The stability of mixtures both during mixing and at elevated temperatures was studied. It was observed that scaling could lead to dangerous reactions, especially when coupled with the degradation of nAl at elevated temperatures. This degradation can be reduced through the reduction of mixture pH, the addition of the inhibitor ADP, or coating of both reactants with an organic acid. Coating both nAl and the metal oxide Bi<sub>2</sub>O<sub>3</sub> with an organic acid improves stability dramatically compared to all other methods tested, with no observed gas production at up to 480 min of exposure to elevated temperatures.

The performance of water processed nanothermites was documented via ESD sensitivity, Parr cell ignition delay time, and pressurization rate. The application of direct-deposited water processed inks on SCB initiators resulted in a decrease in device initiation threshold of over 25% with smaller threshold spreads as compared to THPP. These resonant mixed water processed nanothermites allowed for the effective deposition of a high performance energetic directly onto devices. A large improvement in performance of SCB initiators was documented and opens the door for application of high solids loading, directly deposited, water processed nanoenergetic inks into other initiators and devices.

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