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Selectively-deposited energetic materials: A feasibility study of the piezoelectric inkjet printing of nanothermites

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ABSTRACT

This work investigated the utility of three piezoelectric inkjet printers as energetic material deposition systems, focusing on the ability of each system to achieve the seamless integration of energetic material into small-scale electronic devices. Aluminum copper (II) oxide nanothermite was deposited using the three deposition systems. The printers were evaluated based on their robustness to energetic ink solids loading, drop formation reliability, drop quality degradation over time, and the energetic performance of the deposited material. These metrics correlate to the feasibility of a deposition system to successfully achieve high sample throughput while maintaining the energetic performance of the printed material. After initial system testing, the PipeJet P9 500 μm pipe was used to demonstrate the successful deposition of nanothermite in varying geometric patterns with micrometer precision. From these samples, preliminary propagation speed measurements were obtained, which showed a correlation between the printed line widths and burning rates.

1. Introduction

With the miniaturization of many engineering components that contain energetic material, there exists a need for manufacturing technologies that are capable of seamlessly functionalizing micro-scale electronics with the reactive or energetic materials. For example, microheating elements, micropower sources [1], micropropulsion systems [2,3], microactuation devices [3], and microinitiators [4,5] all require robust electronic packages with precisely located energy sources. These devices pose manufacturing challenges due to the lack of techniques suitable for the micrometer-scale deposition of energetic material. This work proposes the use of piezoelectric inkjet printing for the selective deposition of energetic materials to allow for a degree of volumetric and spatial control that is not obtainable with current energetic material deposition methods. This control will permit the integration of electronics with energetic material, opening the door for a multitude of micro-energetic applications.

Nano-energetic materials have been shown to be useful for MEMS applications and thus have been widely studied for a number of years [6,7]. Within this class of materials, nanothermites are gaining popularity for their notable, highly-exothermic reactions and relatively simple synthesis processes [7]. Nanothermites also offer significant energy density, which can be advantageous when integrating energetic materials into small areas. Currently, solutions for the deposition of energetic material include electrophoresis [8], magnetron sputtering [9], and doctor blade casting [10]. These methods allow for the bulk deposition of energetic materials on a substrate but lack sub-millimeter spatial control. Because of this, basic geometries, which are necessary for the integration of energetic material into electronics, are difficult to achieve with these methods.

Across many industries, inkjet printing has proven to be beneficial for the small-scale deposition of functional inks for fabricating components including metallic nanoparticles [11], carbon nanotubes functionalized with DNA [12], and/or hydrogels [13]. Extensive reviews of current micro- and nano-scale printing technologies have been conducted [14,15]. Of the many inkjet printing systems one could choose from, piezoelectric inkjet printing is advantageous due to the flexibility of ink composition that this print head design allows. In this approach, nozzles are actuated by the change in shape of a piezoelectric material. Reservoirs are either squeezed, bent, or pushed based on their design [16]. In contrast to a thermal inkjet head, which uses flash boiling to produce droplets [16], piezoelectric inkjet printing achieves

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droplets without affecting the ink thermally. This is potentially safer and more reliable for sensitive ink compositions, including energetic materials.

Previous work has utilized inkjet printing for the deposition of small quantities of energetic material for the development of trace vapor calibration tools [17,18]. These samples were not necessarily intended for energetic performance but instead were manufactured as standard test samples for sensor performance validation. There has also been investigation into the effect of ink deposition parameters on the morphological changes of cyclotrimethylenetrinitramine (RDX) [19]. Initial studies of inkjet printing as a deposition method for nanothermites, on a scale that allows for reaction rather than just detection, have been conducted [20–22]. These initial works demonstrated multi-layer, single width lines of printed nanothermites on glass slides with high ignition fidelity; however, they did not study the effects of geometric or printer parameter variation on combustion performance.

This work further investigates the use of piezoeletric inkjet printing of nanothermites as a suitable method for the controlled deposition of energetic material for the development of samples with functional geometric features. It explores the utility of three deposition systems in the precise spatial and volumetric control of deposited aluminum copper (II) oxide. The systems are evaluated for drop formation reliability, robustness to high ink solids loading, and the ignition fidelity of the printed energetic material. In addition, the work demonstrates the energetic performance of the printed samples as characterized by propagation speed measurements. This class of measurement is widely used as an initial metric for nanothermite performance evaluation [8,23,24]. Finally, this work demonstrates a deposition system that allows for printed material flexibility and the spatial control of deposited energetic material, as well as the integration of energetic material with small-scale components such as electronics.

2. Materials and methods

2.1. Material preparation

Due to its thermal stability, aluminum copper (II) oxide nanothermite was formulated as an energetic ink to test the capabilities of several commercial deposition systems. To prepare the material, copper (II) oxide nanoparticles (Sigma Aldrich, 50 nm) were mixed with aluminum nanoparticles (NovaCentrix, 80 nm, 82% active aluminum) and suspended in a solution of dimethylformamide (DMF) and polyvinylpyrrolidone (PVP), a surfactant.

The nanoparticles were mixed at stoichiometric ratios per the ideal reaction:

$$2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$$

and placed in a 10 mL syringe (BD, slip tip) [25]. DMF with 0.5% by weight PVP was added to the syringe to achieve an 8% solids loading. Airtech Flashbreaker 1 tape was placed over the tip of the syringe to prevent leaking. The syringe was then loaded into a custom polytetrafluoroethylene (PTFE) holder and secured on a LabRAM resonant mixer (Resodyn Acoustic Mixer, Inc.). The syringe was mixed at 80% intensity for 16 min and inverted after 8 min [25]. After mixing was complete, the contents of the syringe were emptied into a 1.5 mL microcentrifuge tube, the material was weighed, and additional DMF was added to achieve a desired solids loading. The tube was sealed and stored until the print process commenced.

This ink formulation was chosen based on the results of a previous study on the viscosity and settling time of aluminum and copper(II) oxide nanoparticles in DMF with various surfactants [26]. It was found that the surfactant concentration that optimized ink stability while limiting the impact on reactivity was 0.5% PVP by weight of the solids. The viscosity of the ink used in these experiments was not tested because of concern for accidental ignition of the energetic material. However, both of the constituents inks of aluminum in DMF with PVP and copper (II) oxide in DMF with PVP had viscosities of 0.862 ± 0.035 mPa s [26]. The surface tension of the aluminum copper (II) oxide ink used herein was 30.5 mN/m as measured with the pendant drop technique using a Ramé-Hart goniometer, model 500.

Immediately before printing, the microcentrifuge tube was suspended in a Branson 1800 sonicating bath (Branson Ultrasonics) for 30 min to redistribute any particles that may have fallen out of suspension. The solution was loaded into the deposition system 5 min after sonication finished.

2.2. Deposition methods

Three deposition systems were tested in this work to determine the most effective process for reliable nanothermite printing. All of these systems are variations of open-end piezoelectric inkjet printers. These print heads consist of an ink reservoir connected to a pump chamber. This chamber includes a piezoelectric actuator that can deliver a prescribed displacement pulse which forces droplets through the nozzle orifice [27].

The three print heads tested in this work were a 70 µm piezoelectric nozzle (MicroDrop MD-K-130), an 80 µm piezoelectric nozzle (MicroFab MJ-AL-01-80), and a 500 µm piezoelectrically-actuated pipette (BioFluidix PipeJet P9). These print heads were mounted above a dual-axis linear positioning stage (Aerotech Planar DL 200-XY, 200 mm travel, 0.5 µm accuracy) as seen in Fig. 1(a). These components were controlled through an in-house developed LabView script. The stage position was integrated with the nozzle firing to fabricate complex geometries.

2.3. Side-view imaging

Each printer was evaluated using side-view drop formation analysis techniques. For the MicroFab and the MicroDrop systems, this was achieved using a 3X 110 mm telecentric lens with a color USB camera (Edmund Optics EO-1312). Specifically, the camera, nozzle, and a light-emitting diode (LED) were applied in series. The LED illuminated the nozzle and droplet at the nozzle firing frequency. Phase shifting the LED strobe allowed for droplet observation at various positions in flight. The BioFluidix PipeJet P9 drop formation was captured with a Black and White (BW) Phantom Camera V 7.3 (Vision Research, Inc.) in series with the back lit nozzle. Printing was recorded at 4000 frames per second (fps) with an exposure time of 240 µs.

2.4. Sample preparation

To validate printed energetic performance, samples were prepared with the PipeJet P9 system due to its reliability. The 500 µm P9 pipe was attached to a 2 cm piece of 1.6 mm inner diameter PTFE tubing. The tubing was secured to a 3 mL luer lock syringe (Terumo) via a barbed socket connector. The syringe was fixed to a back pressure regulation system (MicroFab) to prevent the undesirable loss of material during the printing process. The nanothermite was deposited on Novele, a mesoporous media which promotes strong adhesion and uniform deposition (NovaCentrix, IJ-220) [29]. This substrate improved geometric control for the printed material because the adhesion prevented the undesirable wetting previously seen on silicon substrates. Further, Novele may be used in final applications. The energetic material was deposited at volumes of 50 nL per drop; this equated to approximately 4.5 µg/drop as calculated from the mass of printed samples with 225, 450, and 675 drops. The samples were printed from a bitmap of a 6 pixel circle with a 25 pixel long line attached. When printing, the pixels corresponded to a single drop and were spaced at 0.6 mm. The circles, approximately 3.6 mm in diameter, were printed to allow for an increased surface area for initiation. The printed lines were approximately 15 mm long. Three line widths of 1, 2, and 3 pixels were printed, approximately 0.8, 1.6 and 2.4 mm wide respectively. Samples of all of