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Additively manufactured (3DP) thermite structures vs conventionally manufactured equivalents.

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ABSTRACT

Research into additive manufacturing (AM) has been steadily expanding over the past five decades. Where once only polymeric materials could be reliably printed, AM has been adapted to print with a range of materials such as biological, metallic, ceramic and even foodstuffs. The advantages of manufacturing in an additive manner include; a) a layer-by-layer approach allows the creation of architecturally complex structures, b) a reduction in weight, c) lessening of waste and d) the ability to create parts that that are otherwise difficult or too costly to produce.

Pyrotechnic materials, including thermites, are used in a wide range of commercial and defence applications. However, hazards present during manufacturing and storage have resulted in major accidents around the world, with subsequent loss of life and in some cases loss of public infrastructure. AM, using a dry powder printing technique means that parts can be manufactured on demand, reducing the need for storage of large volumes of fully formed products or mixes, thus increasing the safety over lifetime of a product.

The performance of pyrotechnics materials is dependent on a number of properties, including chemical composition, thermodynamic properties and physical form. In combination with composition, architecture could be utilised to understand and control these properties. A bespoke printer capable of additively manufacturing pyrotechnic materials has been constructed with the aim to explore this research area.

In this presentation, we compare the burn rates of AM thermites and compare them to conventionally fabricated compositions and discuss the effects of the print parameters and confinement. We conclude with the results from the burning of AM thermite structures and compare their performance with conventionally prepared equivalent thermite examples.

INTRODUCTION

The additive manufacture of energetic materials is an exciting and growing field.[1] The introduction of this manufacturing technique to the energetics field opens avenues to increase safety, reduce waste and explore a new architectural space. Thermites a specific type of pyrotechnic material are of interest for several reasons. With high temperature self-sustained combustion, their application is quite diverse, in particular, with interest in their use as green primers,[2] land mine clearance and breaching materials[3]. However, thermites can be hard to ignite, requiring a high energy input and can be the cause of failure in multicomponent systems.

The additive manufacture of thermites has been reported as early as 2012,[4] since then there has been a slow and steady increase in research reported in the area with an acceleration in the knowledge in the past five or so years.[5–19] Most reported manufacturing methods focus on direct inkjet writing the thermite, taking an ink and depositing on the print bed. Though this is an effective method of manufacture, many pyrotechnics manufactures are reluctant to implement new process that involve major reformulation or special inks. This study reports on the performance of thermites fabricated with a novel variation of Dry Powder additive manufacturing.

EXPERIMENTAL

Thermite Manufacture

Five different Al/Fe_2O_3 thermites were manufactured with differing particle sizes and shapes, as reported in Table 1. Particle sizes were determined on a CILAS PSA (particle size analyser) and particle morphology determined with the use of a Hitachi SU3500 SEM (scanning electron microscope).

Table 1. The different thermites and their associated aluminium powders, initial aluminium numbers are according to expected d50 values as stated by the manufacturers.

Thermite Code	Aluminium	D[4,3] Mean Diameter / µm	D50 Particle Diameter / µm	Particle Shape[a]
1SAl06Fe2O	Al06	8.5 ± 0.2	7.7 ± 0.1	Rounded
1SAl15Fe2O	Al15	20.7 ± 0.4	18.6 ± 0.3	Rounded
1SAl20Fe2O	Al20	26.9 ± 0.5	25.3 ± 0.4	Rounded
1SAl45Fe2O	Al45	16.6 ± 0.3	14.5 ± 0.2	Flaked
1SAl74Fe2O	Al74	41.7 ± 0.2	37.6 ± 0.2	Rounded

Thermite ingredients (aluminium, varying particle size, and iron (III) oxide) were weighed into a beaker then sieve mixed through progressively smaller sieves. Once sieve mixing of the appropriate composition was complete, the thermites were either tapped or tamped into an acrylic burn tube, or if additively manufactured, inserted into the acrylic burn tube, as shown in Figure 1. AM of the thermites was performed using a dry powder method, the details of which will be reported in forthcoming publications.

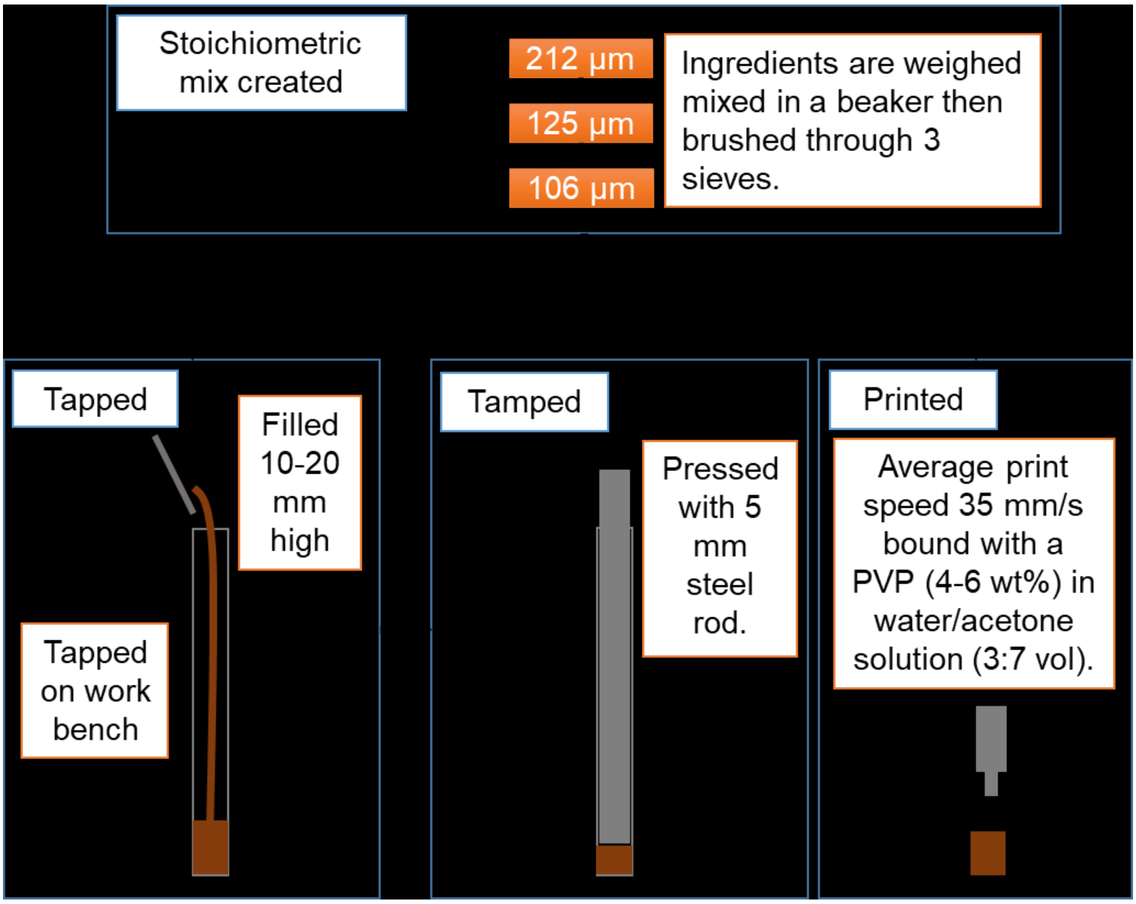

Figure 1. Schematic showing the different types of burn tubes that were assembled. From left to right: tapped, tamped and printed.

Combustion Velocity Measurements

Acrylic tubes with, 3, 5 and 7 mm inner diameter, 100 mm in length, with six ports for fibre optic cables were assembled. The fibre optics were inserted into drilled 2.2 mm holes, pushed flush from the tube inner, then secured in place using Loctite double bubble epoxy adhesive at 25, 35, 45, 55, 65 and 75 mm along the length of the tube, Figure 2. Data from the fibre optics was collected on a DPO2004B Tetronix Oscilloscope, whilst video of the test was collected on a GoPro Hero 8.

Figure 2: Typical Acrylic burn tube, this tube has a 7 mm inner diameter and 100 mm length.

Binder doped samples

To enable more informative comparison of conventional and additively manufactured thermite, two types of binder doped samples were prepared. The first type, solid binder of known weight was mixed with dry powder. The second the binder solution was prepared, added to thermite powder, left to dry then gently ground in a pestle and mortar until powdered. The binder compositions are given in Table 2. The binders used were Polyvinyl Pyrrolidone (PVP) and Cellulose Acetyl Butyrate (CAB).

Table 2. Solid and solution binder mass percentages for the binder doped samples prepared for burn tubes.

Thermite	PVP / wt %		CAB / wt %	
	Solid	Solution	Solid	Solution
1SAl06Fe2O-2	5	2.5, 5	5	5, 7.5
1SAl15Fe2O-2	5	2.5, 5	5	5, 7.5
1SAl45Fe2O-3	5	5, 7.5	5	2.5, 5
1SAl74Fe2O-3	5	5, 7.5	5	2.5, 5

RESULTS AND DISCUSSION

Effect of print parameters and confinement

To identify the effect of confinement on printed parts, five printed thermites were stood on end and an electric match taped on top of each of them. Additionally, one of the printed thermites was entirely covered with an electrical tape. All parts were ignited and showed sustained combustion through the part, Table 3.**Error! Reference source not found.** shows the combustion velocities for these parts and compared to those burnt within a burn tube.

Table 3. Combustion velocities for varied prints of Al/Fe2O3, confined and unconfined, with varying amounts of binder.

Thermite	Tube or Free-standing	PVP in Binder Solution (Binder Duty)/ %	TMD%	Combustion Velocity/ mm s^{-1}
1SAl15Fe2O	FS	4 (10)	30.54	51.66
1SAl15Fe2O	FS	6 (10)	30.50	30.59
1SAl15Fe2O	T	4 (10)	29.32	112.9
1SAl20Fe2O	FS	5 (5)	35.02	48.46
1SAl20Fe2O	T	5 (5)	29.59[a]	104.1
1SAl74Fe2O	FS	6 (10)	33.82	7.535
1SAl74Fe2O	b	4 (5)	33.42	79.24
1SAl74Fe2O	T	4 (10)	32.11	71.75
1SAl74Fe2O	T	4 (5)	23.87[c]	75.79

[a] Reduced pressure in binding system 0.5 bar compared to print above at 1 bar
[b] Sample not freestanding or in tube, covered with electrical tape.
[c] Alternate print file where 4 of the 22 layers are unbound.

Thermite 1SAl15Fe2O was printed twice, one with a 4 % PVP binder and one with 10 % binder duty, one of the parts was loaded into a tube whilst the other was placed vertically against a wooden block and then burned. Both parts have a TMD around 30 %, their combustion velocities however differ greatly with the confined part (in a burn tube) burning at more than twice the speed of the unconfined sample. Although there is a difference in the print parameters for the 1SAl20Fe2O thermite parts, reflected in their differing TMDs, there is a still a more than doubling of combustion velocity when the part is confined compared to unconfined.

The most drastic increase in combustion velocity for being confined vs unconfined is that for 1SAl74Fe2O, with the confined prints demonstrating burns ten times that of unconfined.

In addition to confinement changing the recorded combustion velocity, there is also an indication from the two 1SAl15Fe2O thermites printed with 4 and 6 % PVP binder solutions that increased binder solution percentages will decrease the combustion velocity of the printed part.

The difference in velocities dependent on the amount of binder used to print the part in addition to whether the test is conducted with or without confinement made it clear that there was a need to standardise the print files and confine the parts when testing for the most accurate comparison between conventional and additively manufactured thermites.

Conventional vs Additive: Density and Combustion Velocity

The printed thermites demonstrated theoretical maximum densities (TMD%) less than that of tamped (approximately 40 TMD%) thermites and greater than tapped (approx. 20 TMD%) thermites at around 30 TMD%, Figure 3**. The coefficient of variation for tapped and tamped samples is around 12% whilst for printed samples is reduced to 5%, this demonstrates an increased repeatability during manufacture. In addition to this, for all printed samples it is consistent (within 6 TMD%), as shown in**

Table 4.

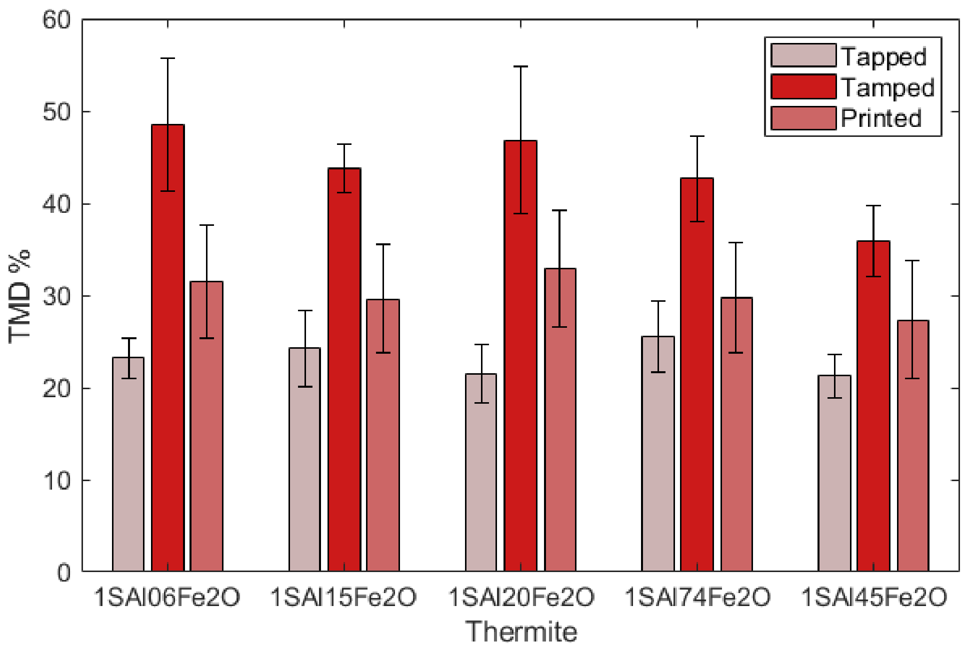

Figure 3. Theoretical maximum density percent (TMD%) for five Al/Fe_2O_3 thermites, tapped, tamped, and printed with PVP binder. Error bars are the standard deviation of the data set.

Table 4. Coefficient of variation in density for tapped, tamped, and printed thermites.

Thermite	Coefficient of Variation / %		
	Tapped	Tamped	Printed
1SAl06Fe2O-1	9.7	14	5.1
1SAl15Fe2O-1	17	6.0	5.1
1SAl20Fe2O-1	15	17	5.2
1SAl45Fe2O-2	11	11	4.2
1SAl74Fe2O-2	15	11	5.0
Mean	13	12	4.9

The density of the printed samples being less than that of tamped and more than that of tapped samples could lead to an expectation that their combustion velocity would lay somewhere between the two conventionally prepared thermites. This is however not the case. When using a PVP binder there is an increase in the combustion velocity of the printed parts, compared to their conventional counterparts. This is true for all particle sizes of aluminium with a significant increase for the thermite using a flake aluminium, Figure 4.

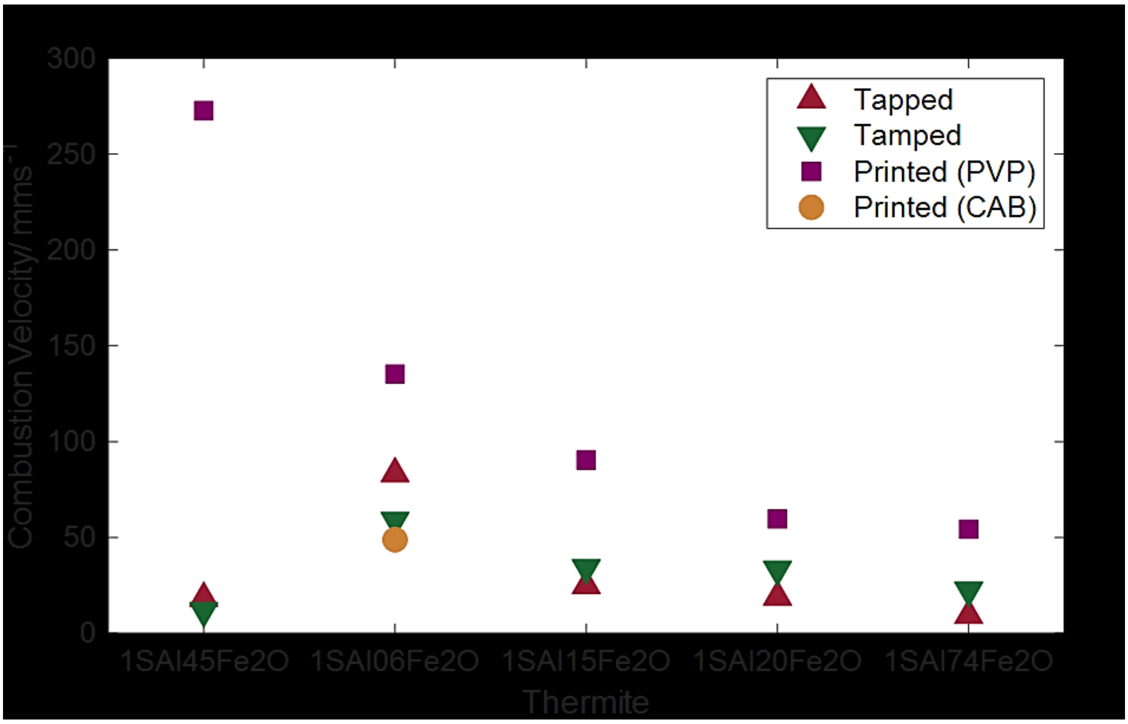

Figure 4. Plot showing the difference in combustion velocity when the thermite is tapped, tamped, or printed. Absence of data for Printed (CAB) is the result of a failure to ignite the samples.

The difference in the combustion velocity, and the failure to ignite when using a different binder, CAB might indicate that the PVP binder is acting as a gas generator aiding in combustion. To test this binder doped samples were prepared. The binder was applied as a solution, then dried for seven days on the bench. The doped thermites were then put into 5 mm tubes to obtain their combustion velocity. They all failed to ignite.

This failure to ignite of most of the Al/Fe_2O_3 samples printed with CAB binder shows that the binder choice will be important for accessing increased combustion velocities at lower TMD%s. the dramatic increase in the combustion velocity seen for the thermite containing flaked aluminium, 1sAl45Fe2O could be the result soft the print orientation, with the flaked particles aligning with the print bed, Allowing the greatest surface area of the particles to be perpendicular to the flame front, Figure 5.

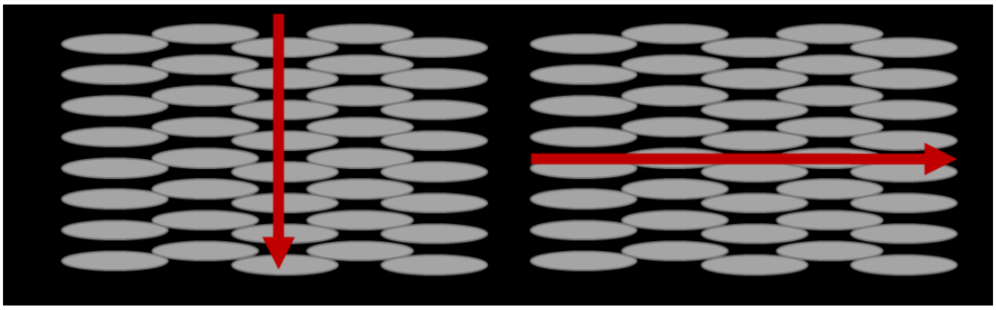

Figure 5. Schematic of the stacking of particles in the a) tapped or tamped tube and the b) printed cylinder. The red arrow shows the direction of the flame front relative to the orientation of the particles.

Conclusions

Additively manufactured samples show a lower coefficient of variation to their conventional counterparts. Their densities are less than tamped samples and greater than tapped samples at approximately 30 % TMD. In addition to showing increased repeatability, printed Al/Fe_2O_3 thermites show increased combustion speeds when printed with a PVP binder. The most dramatic increase in combustion velocity can be seen for 1SAl45Fe2O a thermite containing a flaked aluminium particle. It is theorised that the print orientation is greatly aiding in this increase in combustion velocity though the aluminium particles aligning parallel to the printing plane.

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