Improving the Efficiency of Metallised Explosives

P.Q. Flower[†], P.A. Steward[† 1], L.R. Bates[†], A.J. Shakesheff[‡], P.W. Reip[‡].
† QinetiQ, MOD Fort Halstead, Sevenoaks, Kent TN14 7BP.
‡ QinetiQ Nanomaterials Ltd., Cody Technology Park, Ively Road, Farnborough, Hants GU14 0LX.

Abstract

Metal powders are added to blast explosives and propellants to act as fuels. In practice, micron-sized aluminium powders are typically used for this purpose since they exhibit appropriate reaction kinetics, are dense (ρ = 2.7 g cm^{-3}), and have a relatively high heat of combustion (31 kJ g^{-1}). However, the reactivity of pure aluminium is such that the surface metal reacts with air (oxygen) and forms the metal oxide – which has no value as a fuel and therefore reduces the efficiency of the aluminium.

More recently, there has been interest in nanometric powders for use as fuels. Such nano-powders show improved ignition kinetics compared to micron-sized particles. However, in comparison to micron-sized particles, nano-particles have large specific surface areas – of the order of 20 m^2 g^{-1}. Since the heat of combustion of the aluminium is independent of particle size, nano-powders therefore suffer from poorer specific energy densities due to the greater proportion of oxide present on the particle surfaces.

In theory, a number of other elements exist in the periodic table that potentially offer higher heats of combustion when compared to aluminium, *eg*, carbon, boron, beryllium, etc. However, most of these elements also have a problem which excludes them from consideration as an aluminium replacement.

Boron has a heat of combustion which is approximately twice that of aluminium and therefore looks promising for use as a fuel. However, boron particles do not burn efficiently since they burn at the particle surface (unlike aluminium which burns in the vapour phase) and the build-up of a viscous oxide layer acts as a barrier to inhibit combustion due to the inability of the fuel and oxiser to mix.

It was postulated that the burning temperature of aluminium might be sufficient to aid boron combustion. A fundamental programme of research was therefore instigated, funded by the UK MOD, which looked at the feasibility of producing ultrafine powders of aluminium-boron alloy – which may eventually be used as fuels in energetic materials.

Two methods of alloy production were investigated: (i) a proprietary high energy process, and (ii) using a unique plasma evaporation-condensation process in QinetiQ Nanomaterials Ltd.

The alloy powders have undergone various methods of performance characterisation and have been shown to offer potentially better performance than typical military specification aluminium powders. The hazard properties of the alloy powders have also been characterised, and the risks associated with processing the powders have been shown to be less than those for a number of different nano-aluminium powders and a flake aluminium powder.

---

[1] To whom correspondence should be addressed.

1. Introduction & Background

Aluminium powders have been used in composite propellants since the middle of the last century and aluminised underwater / air high-blast explosives were developed for use in the Second Word War. More recently, research interest in aluminium powders has been rejuvenated by the development of techniques for the preparation of useable quantities of ultrafine and nanometric powders with mean particle sizes of less than one micron and in some instances as low as ten nanometres.

Aluminium powders are added to blast explosives and propellants to act as fuels. In practice, micron-sized aluminium powders are typically used for this purpose since they exhibit appropriate reaction rate kinetics, are dense (ρ = 2.7 g cm^{-3}), and have a relatively high heat of combustion (ΔH_c = -31 kJ g^{-1}). (This compares to -4.2 kJ g^{-1} and -6.3 kJ g^{-1} for TNT and RDX, respectively, burning without air, or -15.1 kJ g^{-1} for TNT burning in air.) However, the reactivity of pure aluminium is such that the surface metal reacts with air (oxygen) and forms a metal oxide shell – which has no value as a fuel and therefore reduces the efficiency of the aluminium.

$$4Al + 3O_2 \xrightarrow{\quad \Delta H_c = \text{-ve} \quad} 2Al_2O_3$$
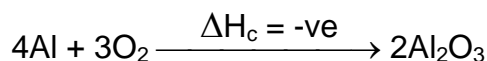
Nano-aluminium powders have the same heat of combustion as micron-sized powders, but show improved ignition kinetics. However, in comparison to micron-sized particles, nano-particles have larger specific surface areas – of the order of 20 to 30 m^2 g^{-1}. Since the heat of combustion of the aluminium is independent of particle size, nano-powders, with their higher surface to volume ratio, therefore suffer from poorer specific energy densities due to the greater proportion of oxide present on the particle surfaces.

It can therefore be seen that the use of aluminium as a fuel in an explosive is not particularly efficient since the surface oxide coating always accounts for a proportion of the added mass. Having said this, the oxide coating is also of benefit since it prevents the readily oxidisable metal from coming into intimate contact with the energetic material during processing and storage.

In theory, a number of other elements exist in the periodic table of the elements that potentially offer similar or higher heats of combustion when compared to aluminium. These include, for example, magnesium, carbon, boron, beryllium, and lithium (Table 1). However, most of these elements also suffer from problems which exclude them from consideration as an aluminium replacement: For example, the burning reaction of carbon is too slow to be of use in the required time frame, whilst beryllium is too toxic and lithium too chemically reactive to be used alongside an explosive material. This leaves Boron, which looks promising since the heat of combustion is almost double that of aluminium. In the open literature on metal fuels for use in energetic materials, boron is described as the 'Holy Grail', but it too has problems.

An advantage of aluminium, which is an additional obstacle when choosing a new material, arises from the fact that aluminium burns in the vapour phase[2], *ie*, it obeys the Glassman criterion which states that for a metal to burn as a vapour, the flame temperature, which equates to the oxide volatilization temperature, must be greater than the temperature of the metal boiling point. For aluminium, the flame (or oxide volatilization) temperature (4000 K) is greater than the metal's boiling point (2791 K).

---

[2] Magnesium also burns in the vapour phase, but it has a lower heat of combustion than aluminium.

Table 1. Heats of combustion of aluminium and its potential replacement fuel powders.

Element	Heat of Combustion (ΔH_c) /kJ g^{-1}	Comment
Magnesium	-25	$\Delta H_c < \Delta H_c$ of Al
Aluminium	-31	Current standard
Carbon	-33	Burning kinetics too slow
Boron	-59	Slow kinetics
Beryllium	-68	Too toxic
Lithium	-86	Too reactive

The fuel is therefore able to escape the particle's oxide shell as the temperature increases. Boron, however, does not obey the Glassman criterion. The boron flame temperature is just 2340 K, whilst it boiling point is 4139 K. Boron therefore burns at the particle surface which then becomes coated in the viscous oxide (B_2O_3). This reduces the ability of the fuel to mix with oxidiser and leads to inefficient burning.

The concept behind this project was that the flame temperature of aluminium (4000 K) is sufficiently close to the boiling point of boron (4193 K) to influence its combustion rate – and that this would be further exploited if the reactivity of the particles was mechanically enhanced and / or the particles were nano-size or nano-phase[3] to improve the ignition kinetics. A fundamental programme of research was therefore instigated, funded by the UK MoD, which looked at the feasibility of producing ultrafine powders of aluminium-boron alloy – which may ultimately be exploited as fuels in energetic materials.

2. Experimental

2.1 Alloy Manufacture

The manufacturing programme set out to produce boron-aluminium mechanical alloys using two processes, supported by a supplementary programme of thermo-chemical computer modelling and experimental characterisation of the alloys.

The initial manufacturing method was a proprietary high energy process expected to produce micron-sized nano-phase mechanical alloys with relatively high numbers of imperfections (*eg*, dislocations, breakages of intermetallic bonds, etc.) [1,2] which, it might be assumed, potentially add to the kinetic energy of the system. Breakage of macrocrystalline material into smaller pieces creates new surfaces, edges and corners at which the atoms are not bonded as strongly as internal atoms. Instead of the normal co-ordination number, some of these atoms may have only 3 or 4 nearest neighbours and will therefore require less energy to bring into the reaction. Whilst this energy may be small when compared to the heat of combustion, and unlikely to influence the thermodynamics of oxidation, the release of this strain energy at a phase transition could, according to the Hedvall effect, alter the chemical reactivity [3]. Dreizin *et al*. [4] have investigated the effect on aluminium-magnesium mechanical alloys and concluded that it is feasible to produce enhanced reactivity alloys with the important benefits of lower ignition temperatures and shorter

---

[3] Nano-phase is used to imply intimate dispersions of one type of nano-sized metal or semi-metal dispersed in a second metal.

combustion times when compared with pure aluminium. It was therefore suggested that the approach may be applicable to the aluminium-boron system.

The high energy process was performed within a glovebox at ambient temperature, to minimise the formation of intermetallic compounds, and under an inert argon atmosphere, to prevent in-process oxidation which would negate the efficiency of the powders as a fuel. The resultant powder effectively consisted of boron particles encapsulated in an aluminium matrix. After processing under argon, it was found that the powders were readily pyrophoric on exposure to air. A range of controlled passivation techniques were therefore studied in order to passivate just the surface of the particles and, as a result, a dry passivation process was developed to render the powders safe to handle.

The nano-phase alloys produced by the high energy process have (i) been characterised for use as a fuel, and (ii) been used as a feedstock for the second method of alloy manufacture: This second method used the unique plasma-evaporation-condensation process available at QinetiQ Nanomaterials Ltd. (QNL). The operating principle of QNL's rigs is that material is fed into the rig, where it is vaporised in a hot plasma zone before being cooled in a way that controls the particle size and structure (Figure 1).
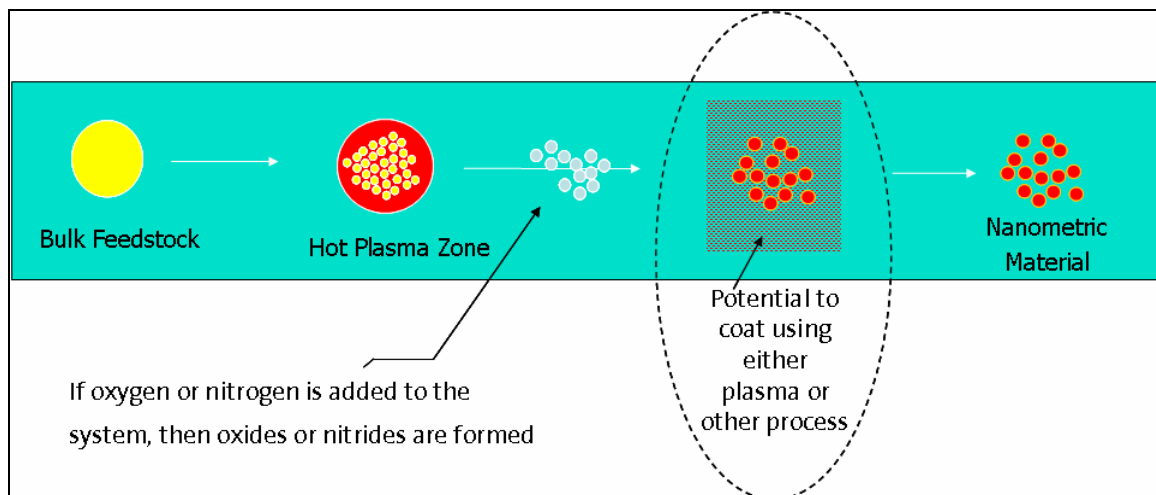
Figure 1. Preparation of nano-powders by plasma evaporation-condensation.

In view of the unknown potential for pyrophoric and explosible hazards presented by aluminium-boron nano-powders, a small explosion resistant powder feed system was specifically developed and manufactured by QNL to enable the powders to be safely processed under an inert atmosphere. The production of the powder was undertaken under an inert argon atmosphere with a controlled amount of oxygen deliberately introduced into the processing equipment to passivate the surface of the powder during production and render the powder safe to handle.

The processing parameters were selected by QNL based on experience gained during the processing of a large range of metal and ceramic powders and proven to result in nanopowders with a primary particle size in the range 20 nm to 100 nm.

In addition to using the aforementioned alloys as a feedstock material for the plasma process, nano-powders were also prepared using a feedstock consisting of micron-sized aluminium powder loosely blended together with micron-sized boron powder.

2.2 Alloy Characterisation

Following manufacture, the alloys were characterised using a range of techniques (although not all data are reported here):

- Particle sizing (laser diffraction), using a Malvern Instruments Mastersizer 2000 to size samples dispersed in water, with the aid of (Dispex) surfactant.

- Explosibility[4] hazard.

- Differential scanning calorimetry (DSC) studies were carried out using a Netzsch DSC 204, heated at a rate of 10° C min^{-1} and operated with a stagnant air atmosphere.

- Semi-micro bomb calorimetry results were obtained using a Parr 1261 calorimeter with a 22 cm^3 semi-micro bomb, using an atmosphere of oxygen at 30 atmospheres pressure, and standardised using benzoic acid.

- X-ray diffraction (XRD).

- Chemical analysis.

- Electron microscopy: The morphology and distribution of the feedstocks and the alloys were characterised by scanning electron microscopy (conventional and field emission) (SEM) and transmission electron microscopy (TEM). TEM samples were prepared by dispersing the powders in ethanol and applying ultra-sonication. A small drop of the dispersion was then taken and placed on to a holey carbon grid. The samples were imaged in a JEOL 4000EX TEM at 400 keV using bright field imaging.

- Accelerating Rate Calorimetry (ARC) – to look for evidence of self-heating.

- Effect of electrostatic discharge (ESD) – performed to determine control measures required when handling the materials.

- Effect of impact & friction mechanical stimuli – performed to provide information on the safe handling of the materials, *eg*, would mechanical stimuli break-up any aggregated particles that my be present and thereby expose un-passivated surfaces which could ignite.

3. Results

3.1 Modelling

It was originally intended that the Cheetah 2 thermochemical modelling code would be used to as a means to determine the optimum ratio of aluminium-to-boron to manufacture. The model was used to examine the predicted detonation performance of compositions using two basic compositions: *ie*, (i) RDX / metal and (ii) RDX / grease / metal, where the metal was a mixture of aluminium and boron.

The results for both compositions showed that alloys with the highest boron content yielded the best performance in terms of total detonation energy. However, this is the expected result given that boron has the higher heat of combustion, and it is known that in practice, this theoretical performance is not realised due to the problems of maintaining boron combustion.

It was therefore concluded from the modelled explosive performance results that the best aluminium-to-boron ratios to aim for would be those with a high boron content of

---

[4] Explosives are said to be…. explosive, whereas powders are said to be explosible.

probably 50% by weight and higher. From the practical point of view and considering that aluminium is the more malleable of the two elements and would be needed to encapsulate the boron, it seemed prudent to start the experimental work at the 50:50 % by weight ratio and proceed from there, gradually increasing the boron content. In practice, however, a wide range of alloy ratios were manufactured.

3.2 Experimental

3.2.1 Bomb calorimetry

The main presumption behind this work programme was to ascertain whether the alloying of aluminium and boron can produce materials that make use of the higher heat of combustion of boron whilst overcoming its unfavourable reaction mechanism and kinetics. The evaluation of the heat of combustion of the alloyed products was thus of paramount interest and the readiness to ignite in the calorimetry experiments would also give information on their suitability for further exploitation.

The initial work with the high energy process alloying technique examined aluminium-to-boron ratios of 75:25, 50:50 and 25:75 atomic weight % (*ie*, 88.2:11.8, 71.4:28.6 and 45.4:54.6 expressed as % weight by weight). The theoretical heats of combustion of these mixtures are given in Table 2.

Table 2. Theoretical heats of combustion of aluminium and boron mixtures.

Al /at.wt %	B /at.wt %	ΔH_c /kJ g^{-1}
100	0	31.3
75	25	34.6
50	50	39.2
25	75	46.4
0	100	58.9

In practice, the 75:25 Al-B alloys burnt well under the experimental conditions with material processed for 8 hours giving the highest heat of combustion of 29.9 kJ g^{-1}, which represents 86.4% of the theoretical value. The boron feedstock used for the initial experiments was not a highly purified grade, with a purity of around 90% boron, so a figure of 86.4% appeared quite respectable. The 50:50 Al-B alloys also burnt well with the material processed for the shortest period of time, 4 hours, giving the highest measured heat of combustion of 35.5 kJ g^{-1}, which is 91% of the theoretical value. Based on these results, it was decided to carry out all future work on the 50:50 at.wt % Al-B alloys.

Late on in the experimental work, a new batch of boron powder was sourced from SB Boron with a specification of 95% to 97% boron content. A repeat batch of the 50:50 Al-B alloyed material was made in the hope that this alloy would show an improved heat of combustion. However, this alloy gave a heat of combustion of 34.3 kJ g^{-1}, which is a disappointing 88% of the theoretical value. However, this material proved to be much more reactive in nature showing a pyrophoric tendency in the non-passivated state.

Although the 50:50 Al-B alloy was only giving around 90% of the theoretical heat of combustion, this was a very encouraging value when compared to Al powder. The best value for the mechanical alloy represents an improvement of 13.4% over the heat of combustion of pure Al. An experimentally determined value for the heat of combustion of Alpoco 5 μm spherical Al was 30.3 kJ g^{-1}, representing 97% of the

theoretical value for aluminium. Therefore the best value for the 50:50 mechanical alloys represents a 17% improvement over an actual Al sample.

3.2.2 Particle size measurement

Laser particle size analysis was conducted on the powder samples dispersed in water using a small addition of Dispex surfactant. The samples were stirred and ultra-sonication applied to reduce agglomeration. Measurements were recorded as both the volume average and number average particle size distributions.
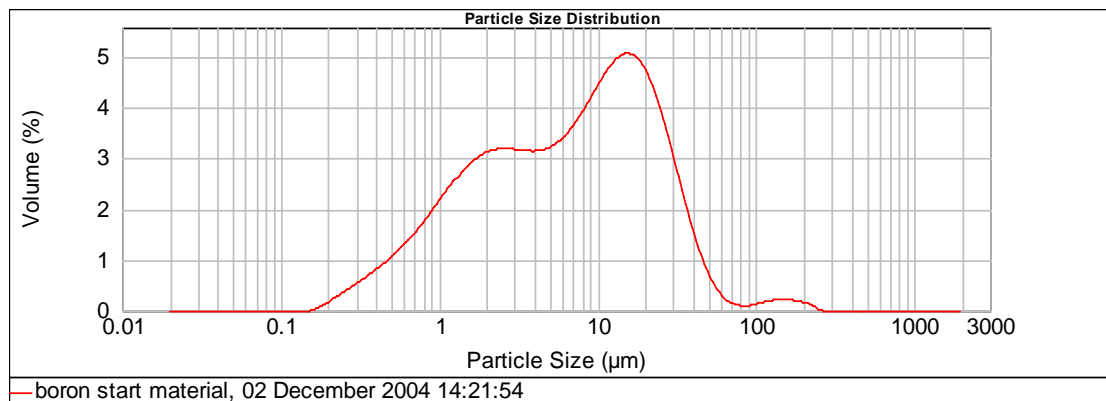
Typical particle size distributions of the feedstock powders are shown in Figure 2 and Figure 3. A normal particle size distribution was obtained for the Al powder with a median particle size of ca 37 µm. The particle size distribution of the B powder exhibited two distinct peaks at ca 2 µm and ca 16 µm and a much wider particle size range between ca 200 nm to ca 200 µm.

The particle size of the high energy process alloy is shown as the volume average distribution in Figure 4. In the volume average mode the median size was 7.2 µm. However, when converted to the number average value, the size distribution showed a high proportion of sub-micron particles.

It was evident that the alloying process led to significant reduction in the particle sizes of the ductile host material. Also, the particle size of the alloy shows the expected fall with increasing processing time. This size reduction would be reflected in increased reactivity of the alloy product.
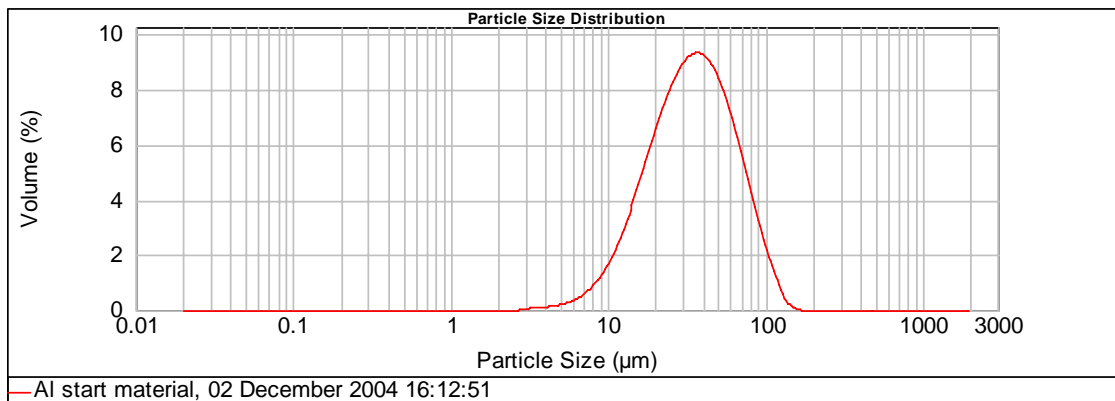
Figure 2. Particle size distribution of the aluminium feedstock.

Figure 3. Particle size distribution of the boron feedstock.
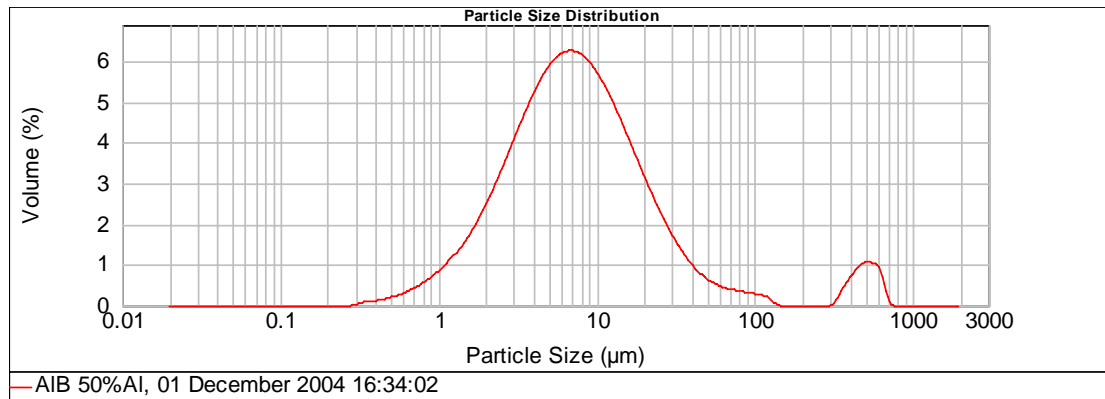
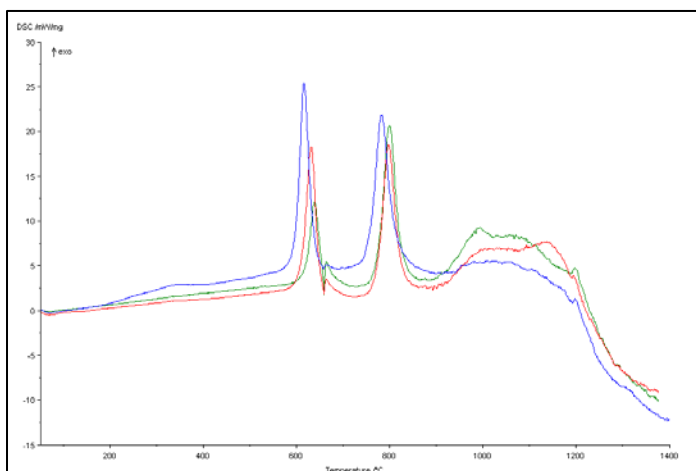**Figure 4.** Particle size distribution of 50:50 at.wt % high energy process alloy.

Plasma processing of the blended Al and B powders yielded particles which were predominantly spherical in shape. Volume average data appeared bi-modal with the bulk of the material at <350 nm, but with the presence of a few large particles between 1 µm and 10 µm. The number average analysis showed only a single peak with a median size of ca 61 nm and the majority of the powder in the range 20 nm to 150 nm.

Particle size was also determined via BET surface area measurements. The high energy process alloy exhibited a specific surface area of 4 m^2 g^{-1} which yields an equivalent spherical diameter of 617 nm. In comparison, the specific surface area of the plasma processed blended material yielded a specific surface area of between 37 and 47 m^2 g^{-1}, corresponding to a particle size of between 53 and 67 nm. Plasma processing of the high energy process alloy yielded a material with a specific surface area of between 22 and 29 m^2 g^{-1}, corresponding to equivalent spherical diameter of between 85 and 110 nm.

More recent work has demonstrated that the nano-particle size can be controlled by changes to the process parameters employed during plasma processing.

3.2.3 Differential scanning calorimetry

Differential scanning calorimetry conducted on samples of the high energy process alloyed powder under a stagnant air atmosphere revealed the presence of two exothermic peaks (Figure 5). The first reaching a peak in the range of 600° to 650° C and corresponding to the oxidation and burning of Al while the second peak occurred at ca 800° C corresponding to the oxidation and burning of B. Slight shifts in the peak positions were evident with differences in processing times.

These DSC results are highly relevant to this programme. DSC work with pure Al and B powders shows no oxidation activity at these low temperatures. The

**Figure 5.** DSC thermograms for alloyed Al-B processed for 4 (green), 12 (red) and 24 (blue) hours.

existence of such profound oxidation behaviour is evidence of the mutual activation of the Al and B caused by the mechanical alloying process. When these materials are incorporated into energetic compositions, such behaviour would manifest itself by an increase in explosive nature, similar to that seen with nanometric Al powder alone.

DSC on the plasma processed material produced from blended powders showed a marked exotherm at ca 800° C, corresponding to the oxidation of B. The Al oxidation exotherm was much smaller and evident at 589° C. A further small peak was evident ca 1036° C, possibly indicative of some aluminium boride. Plasma process material produced from the high energy process alloy feedstock exhibited significantly different traces with two significant, but lower energy, peaks at 600° C and 800° C.
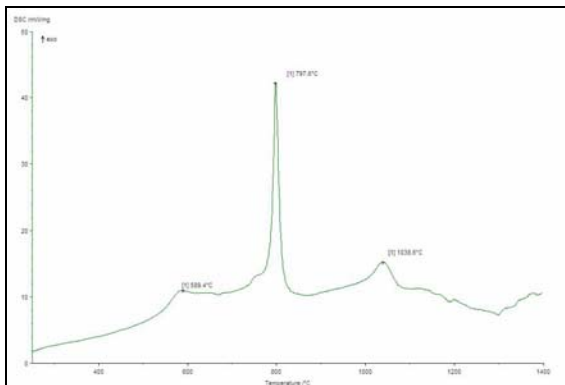
Figure 6. Blended feedstock.
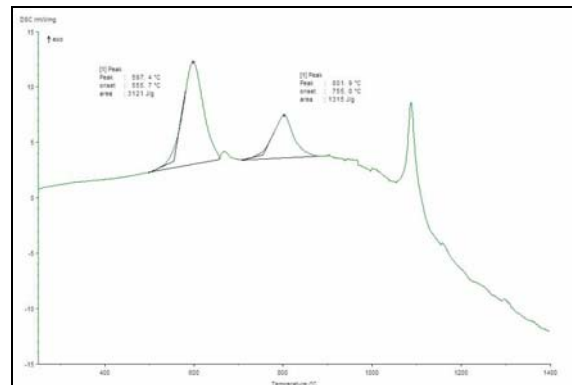

Figure 7. Alloy feedstock.

3.2.4 X-ray diffraction

X-ray diffraction studies on the different compositional variants after processing for 12 hours confirmed the presence of B and that the intensity of the peaks increased with increasing B content. There was no apparent evidence of intermetallic compounds formed between the Al and the B powder after using the high energy processing technique. The plasma processed material possibly revealed the presence of AlB_2 and Al_2O_3, although it was difficult to distinguish between AlB_2 and Al owing to their similar peak angles.

3.2.5 Electron microscopy

A micro-section through a high energy process alloyed granule viewed under backscattered electron microscopy showed the presence of a fine distribution of B particles encapsulated by an Al matrix.

TEM analysis of the plasma processed material made from the blended feedstock showed a crystalline spherical product with some surface irregularity. There was no evidence of a core-shell-like structure, although only a small quantity was sampled. Powder produced from the alloy feedstock also appeared spherical in shape and exhibited variable powder particle sizes – typically < 100 nm, but with some particles as large as 500 nm. Again surfaces were typically irregular, and there was some evidence of lattice fringes (Figure 8) appearing to extend to the surface. This suggests no core-shell structure. However, there was conflicting evidence – with some core-shell structure visible in other TEMs of larger particles (Figure 9).
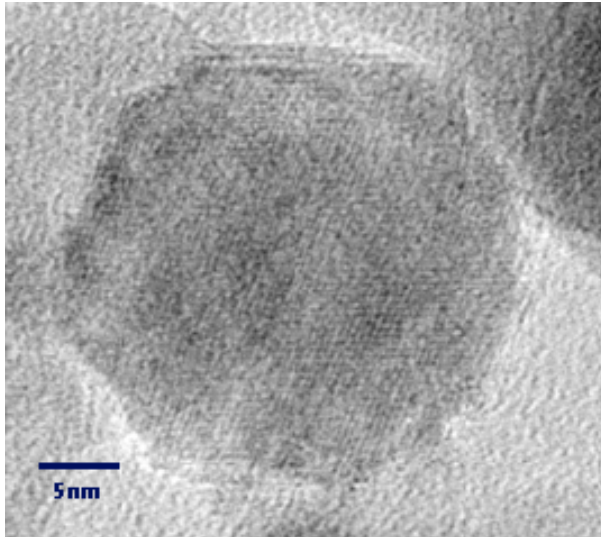
Figure 8. Lattice fringes appearing to extend to particle surface.
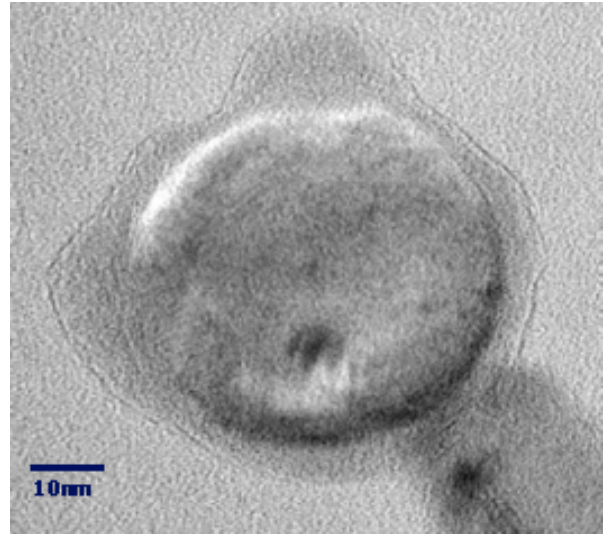
Figure 9. Core-shell particle.

3.2.6 ARC Test

Accelerating rate calorimetry showed no evidence of self-heating until a temperature of 48° C was reached, at which point self-heating of a level just above the detection threshold was seen. After this, the sample / bomb assembly exhibited gradually accelerating self-heating behaviour until the experimental ceiling temperature of 405° C was reached. This was sporadic, with an apparent acceleration occurring at around 164° C. There was no loss of control and no ignition – the maximum heating rate was 3.6° C min^{-1}, recorded at the end of the test. However, an important influence on the reaction was the rate that air could enter the bomb through the ¼" feed tube and it was assumed that this would increasingly become the rate limiting process at higher temperatures, rather than the reactive nature of the sample.

3.2.6 Explosibility Hazard Tests

Dust explosion testing was conducted on a batch of high energy process alloyed powder (50:50 at.wt % Al-B) in order to provide data for risk assessment purposes. The data are summarised in Table 3.

Table 3. High energy process (50:50 at.wt %) Al-B explosibility data.

Parameter	Test Results
Dust Explosion Risk	
Explosion severity (20 litre sphere):	
Maximum explosion pressure, P_{max}	8.6 bar
K_{st} value	180 bar m s^{-1}
St class	1
Minimum ignition energy ("MIE")	25 – 30 mJ
Minimum (dust cloud) ignition temperature ("MIT")	610° C
Limiting Oxygen Concentration ("LOC")	4 % by volume
Thermal Stability Characterisation	
Layer (5 mm layer) Ignition Temperature ("LIT")	340° C

A sample of the passivated 50:50 at.wt % Al-B high energy process alloy was also subjected to a range of EMTAP small-scale explosive hazard test procedures [5]. The results showed that the passivated aluminium-boron alloy was comparatively insensitive to impact and friction. Sensitiveness of metal powders to ESD can be

dependent on whether they are confined or not, re: EMTAP Tests 6 or 7, respectively. The alloy powders, however, gave no ignitions in either test at the highest energy level (4.5 J and 40 mJ, respectively).

4. Discussion & conclusions

It has been demonstrated that ultrafine aluminium-boron mechanical alloys can be made successfully, in kilogram quantities, using (i) a proprietary high energy processing technique that is both low technology and low risk, and (ii) a novel plasma-evaporation-condensation processing technique. Both processes are readily capable of being scaled-up to manufacture larger quantities of material.

The characterisation of the resultant materials, as reported here, shows their important properties. The purpose behind the concept of making these alloys is to produce fuels for use in explosive formulations which are more energetic, theoretically giving rise to more powerful blast explosives and propellants. To achieve this goal, the alloys must display greater heats of combustion than the commonly used military standard aluminium powders. But this extra energy is of no use unless it can be released rapidly during the lifetime of the explosion process, *ie*, they must display appropriate reaction kinetics and mechanism in their oxidation process.

Both of these requirements have been proved in this initial work. The 50:50 at.wt % high-energy-process alloy has been measured to give a heat of combustion 13.4% greater than the theoretical value for pure aluminium and 17% greater than the value for an actual aluminium powder that has been used in explosive formulation work.

The DSC work has also shown qualitatively the vastly increased reactivity of the alloy towards aerial oxidation compared to elemental aluminium and boron powders.

Microscopy has shown that the alloy material is composed of boron powder finely dispersed in an aluminium matrix, and X-ray analysis has confirmed that there is little or no evidence of aluminium boride compound formation.

Hazard testing and accelerating rate calorimetry have both confirmed that handling suitably passivated powders produced by the high energy process should be no more hazardous than comparable aluminium powders.

5. Acknowledgments

5. References

1. Garner W.E. (Ed.) Chemistry of the Solid State. Butterworths, London, (1955).
2. McLain J.H. Pyrotechnics. The Franklin Institute Press, Philadelphia, (1960).
3. Hedvall J.A. Solid State Chemistry, Whence, Where & Whither. Elsevier, London (1996).
4. Dreizin E.L. *et al*. Preparation and Characterisation of Energetic Al-Mg Mechanical Alloy Powders. Combustion and Flame, 128, 259-269 (2002).
5. Defence Ordnance Safety Group, Energetic Materials Testing & Assessment Policy Committee, Manual of Tests, Issue 2 (April 2005).