The effect of Si-Bi$_2$O$_3$ on the ignition of the Al-CuO thermite

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The effect of Si-Bi$_2$O$_3$ and particle size on the ignition of the Al-CuO thermite

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Abstract

The ignition temperature of the Al-CuO thermite was measured using DTA at a scan rate of 50 °C.min^{-1} in a nitrogen atmosphere. Thermite reactions are difficult to start as they require very high temperatures for ignition, e.g. for Al-CuO thermite comprising micron particles it is ca. 940 °C. It was found that the ignition temperature is significantly reduced when the binary Si-Bi$_2$O$_3$ system is added as sensitizer. Further improvement is achieved when the reagents are nano-sized powders. For the composition Al + CuO + Si + Bi$_2$O$_3$ (65.3:14.7:16:4 wt %), with all components nano-sized, the observed ignition temperature is ca. 613 °C and a thermal runaway reaction is observed in the DTA.

Key words: Pyrotechnics; Thermite; Ignition temperature; Nanoparticles

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1. Introduction

Pyrotechnic compositions are mixtures of solid fuel(s) with solid oxidizer(s) capable of a self-sustaining combustion. Thermites are a subclass of pyrotechnic reactions characterized by a very large heat release [1, 2]. The aluminium + iron oxide system represents the archetype thermite reaction. Table 1 lists representative thermite reactions. The adiabatic reaction temperature provides a quantitative measure of exothermicity. In thermites this temperature exceeds the melting point of at least one of the products [2]. The 2Al + 3CuO thermite is particularly interesting as the adiabatic temperature is sufficient to vapourize part of the copper metal formed by the reduction of the oxide.

Thermite-type reactions can be ignited by a combustion wave from a chemical reaction, an electric current, radiation energy from a laser beam or by mechanical impact [3]. Following ignition, propagation proceeds in a layer-to-layer fashion. During combustion, some constituents may remain in the solid state, while others may melt, vaporise, and/or decompose to yield some gaseous species. Thus the heat transfer mechanisms responsible for propagation include radiation, convection, and conduction [4].

The rate of combustion of pyrotechnic compositions is affected by numerous variables. The nature of the fuel and the oxidant, the mixture stoichiometry, particle size and distribution and the quality of mixing are the most important [5]. Optimum performance is generally expected for near-stoichiometric compositions because they ignite and propagate more readily [5]. In general, decreasing the particle size of the reactants increases the combustion rate [2, 6]. Conversion and reaction rate are affected by the contact quality and contact area between reactant powders [7]. Thus good dispersive mixing, to ensure powder homogeneity, is crucial for efficient and reliable combustion [3, 8, 9]. Good dispersion and mixing of nano-reactants is also essential for achieving maximum burning rates in a pyrotechnic mixture [10].

Traditionally, composite energetic materials were prepared by physically mixing the fine dry powders of fuel(s) and oxidant(s). Mixing nanoparticles of metal and oxidizer by such conventional means can present an extreme fire hazard. Valliappan *et al.* [10] developed a method in which very fine powder components of composite energetic material are dispersed and mixed in an organic solvent. At the nanometer scale, particle interactions become significantly more influential because of a higher tendency to agglomerate [11].

Thermite reactions utilizing micron-sized aluminium powder fuels feature long ignition delays, slow burning rates and incomplete combustion [12]. Aluminium melts at ca. 660 °C but ignition requires much higher temperatures especially when the oxidizer has an elevated melting- or decomposition temperature. Often the required ignition temperature cannot be reached with conventional ignition sources [2]. The combustion of conventional thermite compositions is rate limited by the slow heterogeneous mass transfer across the metal and oxide interface [13]. The relatively low reaction rate, and the fact that they are not easy to ignite, have restricted practical applications of conventional pyrotechnic reactions.

Adding small amounts aluminium fluorite or cryolite ($NaAlF_6$) reduces the ignition temperature and can double the burn rate [2]. These performance improvements are attributed to the salts removing the inert reaction-inhibiting alumina coating on the aluminium at temperatures significantly lower than the ignition temperature [2].

Reducing the fuel particle size into the nanometer range is much more effective as the interface area is substantially increased [13, 14, 15]. The use of nano-aluminium as fuel enhances ignition sensitivity, i.e. it reduces ignition delay and lowers the ignition temperature [13, 16, 17]. Granier and Pantoya [16] attribute this to the increased surface energy associated with nanoparticles, an effect that also leads to a reduction in the melting point. Substituting micrometer-sized Al with nano-sized Al particles also changes the kinetic mechanism of the combustion reaction [18]: While flame speed increases with density for micron-scale Al particle compositions, the opposite is observed for nanoscale aluminium particle mixtures [19]. The high combustion velocity (reaching 1000 m.s^{-1}), observed for nano-scale thermites [14, 15], suggests that strong convective mechanisms operate in flame propagation [4, 15].

Sanders *et al*. [20] studied the modes of combustion and reaction behaviour of several Al-based nanoscale-thermites including Al + CuO. They found a correlation between the maximum pressure output and optimum propagation speed (or burn rate). The propagation speed depends on gas production and on the thermodynamic state of the products. Their results suggest that condensing gases or solidifying liquids greatly enhance heat transfer rates. At low compaction densities the propagation wave is supersonic with respect to the mixture sound speed. However it decreases with density in contradiction to classical detonation behaviour. This means that a different propagation mechanism is operative [19, 20].

Bare nano-sized aluminium particles are pyrophoric. However, an oxide layer, typically 4 to 8 nm thick, readily forms and it reduces the ignition sensitivity in air. This passivation shell can become an appreciable portion of the total material when the particle size approaches nanometer dimensions [16]. Levitas *et al*. [21] proposed the following mechanism to explain the fast oxidation of Al nanoparticles. The thin oxide skins on the outside of the particles represent rigid pressure vessel walls. Melting of the metal is associated by a significant lowering of density. However, the confinement by the oxide layer, checks the required expansion and this induces pressures reaching values in the GPa range. Eventually catastrophic spallation of the oxide shell takes place. The subsequent unloading wave violently disperses liquid aluminium clusters so that, in contrast to traditional mechanisms, the oxidation is not limited by diffusion.

A major benefit of thermite reactions are their immunity to accidental ignition [22]. This makes them particularly interesting as replacement candidates for primary explosives in conventional detonators [23]. However, in this application superfast combustion and easier ignition are desired. The discussion presented above amply demonstrates that nano-sized aluminium powder imparts improved ignition sensitivity and greatly enhances the energy release rate of thermites. In fact, Moore *et al*. [24] showed that even a partial substitution (≈ 20 wt %) of micron-sized fuel in the $Al + MoO_3$ thermite is sufficient to reduce the ignition delay times by up to two orders of magnitude and to dramatically increase the combustion velocity. This communication explores further sensitization of the $Al + CuO$ thermite reaction [25] by the fast-burning $Si + Bi_2O_3$ pyrotechnic composition [26, 27]. DTA ignition studies are used to show that the ignition temperature can be reduced significantly even when micron-sized aluminium fuel is retained.

2. Experimental

2.1 Materials

This study considered both micrometer-sized (denoted as "micron" or "coarse" herein) and nano-sized particles (labelled "nano" herein). Figure 1 shows SEM pictures of the various powders. Aluminium was used as the energetic fuel. Micrometer-sized tuber-shaped aluminium powder (< 25 μm) was supplied by PAL Chemicals. Aluminium flakes with thickness on the nanometre scale were supplied by CSIR. These flakes contained 3 wt % of a proprietary organic

coating. The aluminium content was 91.5 wt %. The flakes actually featured micrometer dimensions but their thickness was in the range 100 nm to 200 nm. The nano-sized silicon powder (< 50 nm, purity > 99%) was obtained from Hefei Kaier. Nano-sized CuO (<50 nm) and Bi_2O_3 (<100 nm, purity >99.9 %) were purchased from Sigma-Aldrich chemicals. The micron CuO was a laboratory grade powder from Merck that was ground finer by ball milling. The micron-sized silicon was Type 4 supplied by Millrox. Micron Bi_2O_3 was prepared by thermal decomposition of bismuth basic carbonate at 460 °C using the method described by Kalombo *et al*. [27].

2.2 Characterisation

Phase identifications were carried out by XRD analysis performed on a PANalytical X'Pert Pro powder diffractometer. The instrument was fitted with an X'Celerator detector and variable divergence- and receiving slits with Mn filtered Fe-Kα radiation (0.193609 nm) operated at 25 kV and 35 mA. The phases were identified using X'Pert Highscore plus software and composition quantified using the Rietveld method.

Cold field emission gun scanning electron microscopes (JOEL JSM-6000F of high magnification and JOEL JSM-840 of low magnification) were used to investigate the morphology of the powders.

Single point BET surface area measurements were done using a Coulter SA 3100 instrument. Particle size determinations were performed using a Malvern Mastersizer Hydro 2000MU instrument. Unfortunately it was not possible to measure the particle sizes of the nano-sized powders.

2.3 Sample preparation

Powder mixtures were dispersed in sufficient cyclohexane to make a thick paste. Particle agglomerates were broken down and mixing effected by grinding in a glass mortar and pestle. Afterwards the solvent was allowed to evaporate at ambient conditions followed by a final drying step in an oven set at 60˚C.

2.4 Thermal analysis

A Shimadzu DTA-50 instrument was used to perform thermal analysis. Alumina sample pans were employed and 5 mg α-Al$_2$O$_3$ was used as reference compound. Two thin copper discs (500 μm thick) were placed at the bottom of the pans. These served to protect the measuring head against the extreme temperature excursions generated by the thermite reactions. Without these discs, severe damage was invariably incurred. Even in the presence of the copper disks, some reactions resulted in a thermal runaway that shattered the alumina pan. The measuring pan was filled with 5 mg thermite composition. The powder was pushed down firmly by hand. Temperature was scanned from ambient to 900 °C or 1000 °C at a scan rate of 50 °C.min^{-1} in a nitrogen atmosphere.

2.5 *Burn rate measurements*

Burn rates were determined in commercial detonator assemblies without the high explosive base charges and with the thermite composition substituting the conventional time delay composition pressed in rigid aluminium elements or custom made steel tubes. The filling of the delay elements and the measurement procedures used were similar to those previously described by Kalombo et al. [27].

3. Results

The BET surface areas and the particle sizes of the powders are given in Table 2. The XRD spectra revealed the following: The silicon and aluminium powders were X-ray pure cubic phases. The CuO powders were monoclinic but the nano powder contained some of the cubic phase and Cu$_2$(OH)$_3$NO$_3$ (orthorhombic) as minor impurities. The micron Bi$_2$O$_3$ was X-ray pure monoclinic phase but the nano Bi$_2$O$_3$ was of the tetragonal phase.

Figure 2 shows the DTA response for a stoichiometric 2Al + 3CuO mixture comprising micron aluminium and nano-sized CuO particles. The first endotherm has an onset temperature of 647 °C and corresponds to the melting of the aluminium metal. The second endotherm with an onset temperature at ca. 894 °C probably corresponds to the melting and dissolution of the CuO in the aluminium melt. This is followed by a fast exotherm. The ignition temperature of the composition under these conditions can be taken as the corresponding onset temperature, i.e. ca. 939 °C in this case. When the CuO was replaced by a stoichiometric amount of nano Bi$_2$O$_3$, the onset temperature was lowered to ca. 801 °C.

The stoichiometric thermite mixture, for the reaction $2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$, contains 18.44 wt % aluminium. A stoichiometric mixture for the sensitizer, defined by the reaction $3Si + 2Bi_2O_3 \rightarrow 3SiO_2 + 4Bi$, contains 7.83 wt % silicon as fuel. However, it was decided to use the fastest burning composition instead. According to Kalombo *et al.* [27], it contains 20 wt % silicon. The effect of particle size was studied using these compositions and the results are listed in Table 3.

Figure 3 shows the DTA response of mixtures containing 80 wt % $2Al + 3CuO$ stoichiometric thermite mixture with 20 wt % of the sensitizer ($Si + Bi_2O_3$). It features much stronger and sharper exothermic peaks (corresponding thermal runaway situations) than the one shown in Figure 2. The onset temperature is 689 °C for the system comprising micron-sized powders. The ignition temperature is lowered to 613 °C if only nano-sized powders are used. In both cases the exotherms shows an extreme temperature rise that far exceeds that observed for the thermite itself. The thermal runaway is so fast that it approaches a "thermal explosion". This is substantiated by the fact that in both cases the alumina sample pans were shattered.

The effect of particle size on the ignition temperature is summarized in Table 3. The ignition temperature of the thermite is about 940 °C irrespective of the particles size of the reactants. The ignition temperature of the $Si + Bi_2O_3$ mixture is affected by particle size. The ignition temperature is 935 °C for a coarse powder mixture. This drops down to about 747 °C when the mixture is composed of nano-sized powders.

Thermal runaway was observed for the sensitized mixtures when the component powders of the thermite were both nano-sized, but also when all the powders used were micron-sized. The ignition temperature for the all-nano mixture was significantly lower ($T_E \approx 613$ °C) than those for the all-coarse mixture ($T_E = 689$ °C) and the all-nano-thermite + all-coarse-sensitizer ($T_E \approx 735$ °C). No thermal runaway was observed for other mixtures shown in Table 3. This may be due to the mismatch in particle sizes resulting in segregation.

Table 4 details the effect of varying the amount of sensitizer on the ignition temperature. Thermal runaway only occurred for the composition containing 20 wt % sensitizer. The lowest ignition temperature was also attained at this sensitizer content. Table 4 also reports on the effect of varying the stoichiometry of the thermite composition. The lowest ignition temperature is attained at the stoichiometric thermite composition. Again, this was the only one that led to a thermal runaway.

The ignition temperature of the stoichiometric mixture of aluminium and bismuth trioxide is quite high as well, i.e. 801 °C (See last entry in Table 4). The onset temperatures for the other compositions listed in Table 4 show that just adding small amounts of either silicon or bismuth trioxide to the thermite only leads to a modest reduction in the ignition temperature. Noteworthy is the fact that adding a substantial quantity of bismuth trioxide did lead to thermal runaway.

Figure 4 reports burn rates for the $CuO + Al$ thermite sensitized by 25 wt % $Si + Bi_2O_3$ using only micron-sized powders. Remarkably, the sensitized $Al + CuO$ composition burns significantly faster than the $Si + Bi_2O_3$ compositions. The burn rate for the thermite composition containing 20 wt % aluminium as fuel is at least on par with fast-burning $Si + Pb_3O_4$ time delay compositions. Detonator blowouts prevented measurement of the burn rate for the stoichiometric mixture of micron-sized $CuO + Al$ thermite sensitized with 20 wt % $Si + Bi_2O_3$. However, replacing the aluminium rigid elements with custom-made steel tubes solved this problem. The burn rate in steel tubes was measured as 655 ± 67 mm/s, i.e. about twice as fast as the fastest composition reported in Figure 4.

4. Discussion

The observations that the burn rate of the quaternary mixture, comprising micron-sized powders, exceeds that of the fast-burning $Si + Bi_2O_3$ system is highly significant. This composition also had a lower ignition temperature. The DSC melting temperature of the aluminium powders were ca. 598 °C and 654 °C for the nano and micron powders respectively. Interestingly, in each case the observed ignition temperatures were slightly higher than the corresponding melting point of the aluminium powder used as fuel. This suggests the following hypothesis for explaining the observed thermal runaway results. In the presence of copper oxide acting as a catalyst, the reaction of the silicon with bismuth oxide is facilitated by the aluminium turning into a liquid. The concomitant energy release provides the required activation energy required to "kick-start" the thermite reaction between the aluminium and the copper oxide allowing it to proceed at an extremely fast rate.

5. Conclusion

The use of Si + Bi$_2$O$_3$ (mass ratio 1:4) as sensitizer for the Al + CuO plus thermite reaction was studied using DTA. The effects of particle size (micron vs. nano), thermite stoichiometry, and the amount of sensitizer were investigated. Thermal runaway was only observed for stoichiometric 2Al + 3CuO thermite composition in the presence of sufficient sensitizer. The lowest ignition temperatures were obtained with stoichiometric thermite mixture containing 20 wt % sensitizer. The ignition temperature was ca. 613 °C when the mixture comprised nano-sized powders. When coarse, micron-sized powders were used instead, the ignition temperature was 689 °C. In both cases the ignition event led to a thermal runaway reaction creating a temperature shock severe enough to cause the disintegration of alumina sample pans. Instead, no thermal runaway is found at a slightly higher sensitizer content of 25 wt %. This system, comprising micron-sized powders, may provide a fast burning replacement alternative for the red lead + silicon system used in millisecond time delays. Lead-based system need to be replaced owing to environmental concerns and the thermite system presents a "greener" option.

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Figure 1. SEM micrographs of A. Micron aluminium; B. Nano aluminium flakes; C. Micron silicon; D. Nano silicon; E. Micron copper oxide; F. Nano copper oxide CuO; G. Micron bismuth trioxide; and H. Nano bismuth trioxide

Figure 2. DTA response of the stoichiometric Al-CuO composition comprising micron aluminium and nano-sized copper oxide particles.

Figure 3. DTA response of the $Al + CuO + Si + Bi_2O_3$ (14.7: 65.3: 4: 16 wt %) system made up with either just micron particles or the nano-sized powders.

Figure 4. Burn rates of the sensitized thermite compared to reported burn rates for the $Bi_2O_3 + Si$ system. −□− Brammer et al. [26]; −△− Kalombo et al. [27]; −O− Varying aluminium fuel content in the $CuO + Al$ thermite sensitized by 25 wt % $Si + Bi_2O_3$.

Table 1. Heat of reaction (Q), adiabatic reaction temperature (T_{ad}), and state of the product metal and oxide of selected thermite reactions [1]

Thermite reaction	Q MJ/kg	T_{ad} °C	State of Oxide	State of Metal
$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$	3.96	2862	liquid	liquid-gas
$2Al + Bi_2O_3 \rightarrow 2Bi + Al_2O_3$	2.11	3046	liquid-gas	gas
$2Al + 3CuO \rightarrow 3Cu + Al_2O_3$	4.08	2570	liquid	liquid-gas
$4Al + 3MnO_2 \rightarrow 3Mn + 2Al_2O_3$	4.85	2645	liquid	gas

Table 2. BET surface area and particle size and of the powders.

Metal	Al		Si		CuO		Bi_2O_3	
Size	nano	micron	nano	micron	nano	micron	nano	micron
BET/ $m^2.g^{-1}$	4.77	0.39	37.1	10.1	17.6	9.25	2.24	0.37
$D_{0.1}/\mu m$	5.12	9.65	-	0.39	-	1.96	-	3.20
$D_{0.5}/\mu m$	18.0	24.3	-	1.39	-	5.76	-	13.8
$D_{0.9}/\mu m$	48.1	55.2	-	63.6	-	25.5	-	33.6

Table 3. Ignition temperatures of mixtures with compositions indicated in wt %

Thermite		Sensitizer		Onset/ignition
81.7	18.3	80	20	temperature,
CuO	Al	Bi_2O_3	Si	$T_E/°C$
micron	micron	-	-	942
nano	micron	-	-	939
nano	nano	-	-	942
-	-	micron	micron	935
-	-	nano	nano	747
Thermite		Sensitizer		Onset/ignition
65.3	14.7	16	4	temperature,
CuO	Al	Bi_2O_3	Si	$T_E/°C$
micron	micron	micron	micron	689[a]
micron	micron	nano	nano	No exotherm
nano	nano	micron	micron	737[a] & 733[a]
nano	micron	nano	nano	727
nano	nano	nano	nano	613[a] & 610[a]

[a]Thermal runaway

Table 4. The effects of (A) sensitizer content; (B) thermite stoichiometry, and (C) other compositions on the onset/ignition temperature. All compositions are indicated in wt %.

|	Thermite			Sensitizer			Onset/ignition temperature, T_e/°C
	Al nano	CuO nano	Total	Si nano	Bi_2O_3 nano	Total	
A	16.6	73.4	**90.0**	2.0	8.0	**10.0**	732
	15.9	69.0	**84.9**	3.0	12.1	**15.1**	623
	14.7	65.3	**80.0**	4.0	16.0	**20.0**	613[a]
	14.0	61.1	**75.1**	5.0	20.0	**25.0**	620
B	20.0	60.0	**80.0**	4.0	16.0	**20.0**	621
	15.9	64.1	**80.0**	4.0	15.9	**19.9**	622
	14.5	65.6	**80.1**	4.0	16.0	**20.0**	610[a]
	12.1	68.0	**80.1**	4.1	15.8	**19.9**	621
C	17.7	78.3	**96.0**	4.0	-	**4.0**	895
	17.0	75.0	**92.0**	8.0	-	**8.0**	884
	15.5	68.3	**83.8**	-	16.2	**16.2**	789
	14.7	64.7	**79.4**	-	20.6	**20.6**	806
	11.7	12.8	**24.5**	-	75.5	**75.5**	734[a]
	10.4	-	**10.4**	-	89.6	**89.6**	801
	6.8	-	**6.8**	14.2	79.0	**93.2**	No exotherm

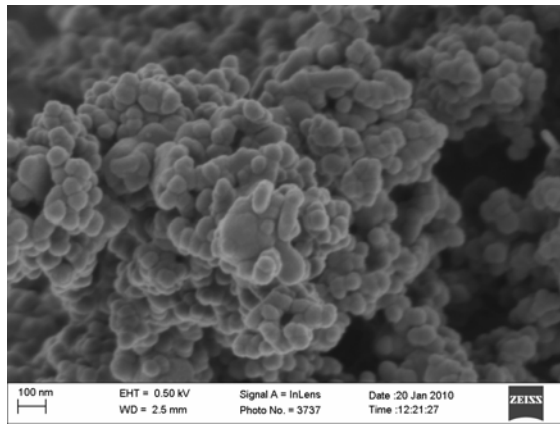[a]Thermal runaway

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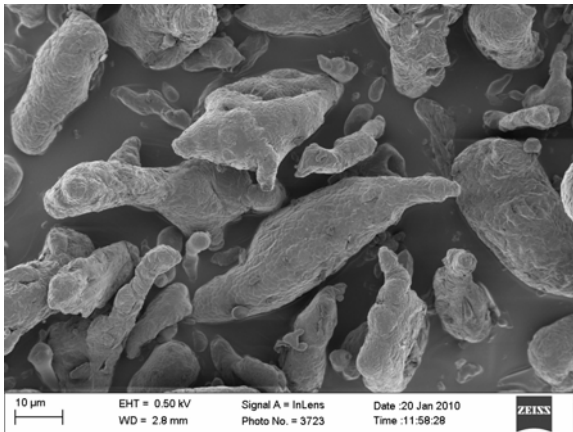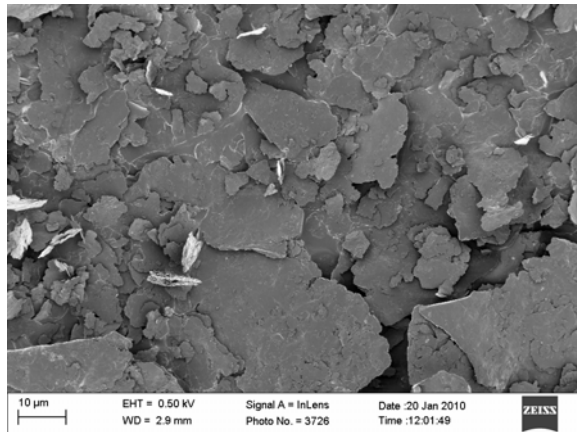
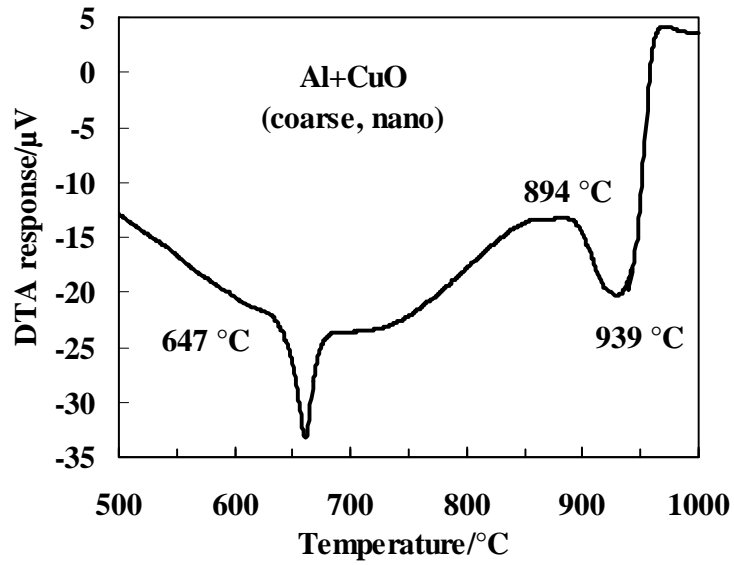A.   Micron aluminium

B.   Nano aluminium flakes
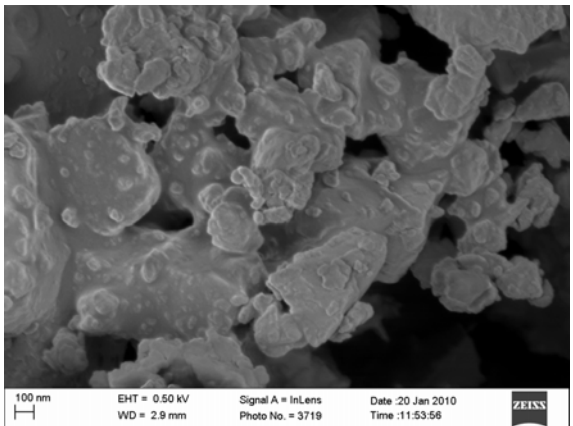

C.   Micron silicon
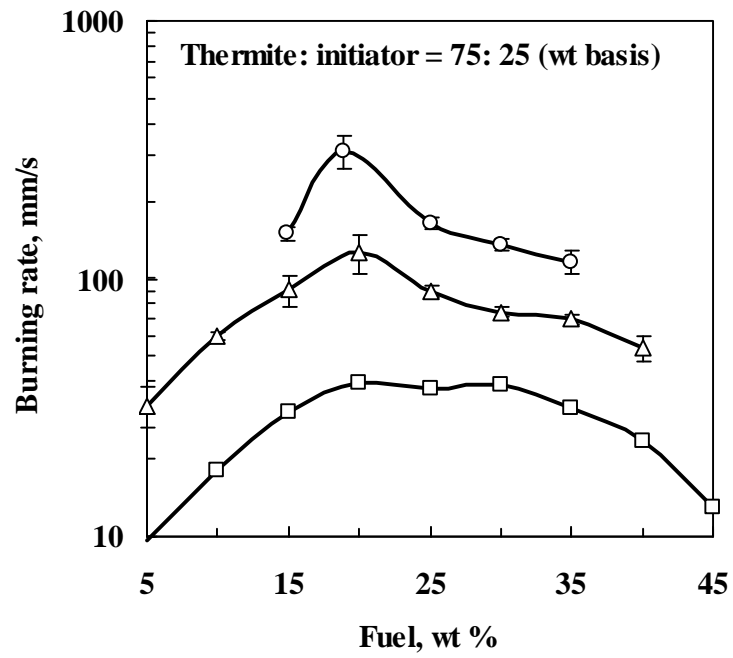

D.   Nano silicon

Figure 1. SEM micrographs of A. Micron aluminium; B. Nano aluminium flakes; C. Micron silicon; D. Nano silicon; E. Micron copper oxide; F. Nano copper oxide CuO; G. Micron bismuth trioxide; and H. Nano bismuth trioxide

Figure 2. DTA response of the stoichiometric Al-CuO composition comprising micron aluminium and nano-sized copper oxide particles.
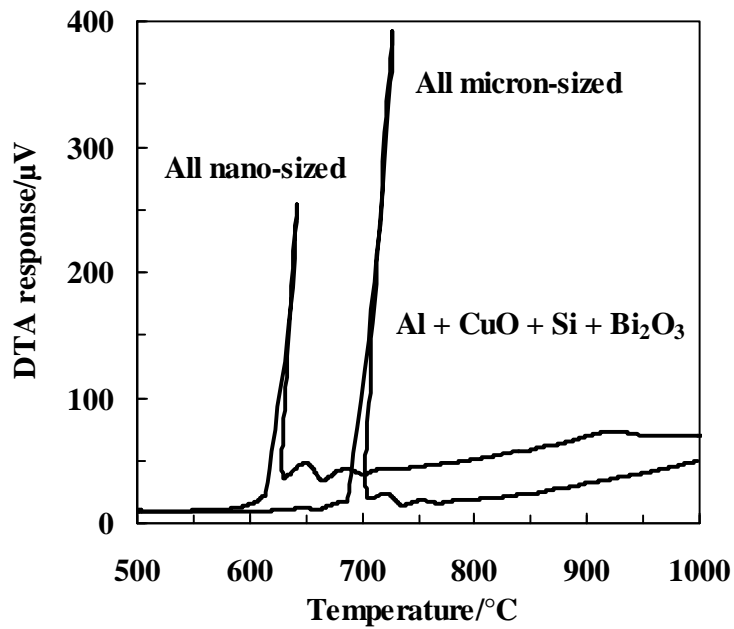
Figure 3. DTA response of the Al + CuO + Si + Bi$_2$O$_3$ (14.7: 65.3: 4: 16 wt %) system made up with either just micron particles or the nano-sized powders.

Figure 4. Burn rates of the sensitized thermite compared to reported burn rates for the Bi_2O_3 + Si system. $-\square-$ Brammer et al. [26]; $-\triangle-$ Kalombo et al. [27]; $-\bigcirc-$ Varying aluminium fuel content in the CuO + Al thermite sensitized by 25 wt % Si + Bi_2O_3.