



# The effect of Si–Bi<sub>2</sub>O<sub>3</sub> 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<sup>-1</sup> 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<sub>2</sub>O<sub>3</sub> system is added as sensitizer. Further improvement is achieved when the reagents are nano-sized powders. For the composition Al + CuO + Si + Bi<sub>2</sub>O<sub>3</sub> (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.

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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 vaporize 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<sub>6</sub>) 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].

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**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	$T_{ad}$	State of	
	MJ/kg	°C	Oxide	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

Reducing the fuel particle size into the nanometer range is much more effective as the interface area is substantially increased [13–15]. 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  $1000 \text{ m s}^{-1}$ ), 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 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 ( $\approx 20 \text{ wt.}\%$ ) 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). Fig. 1 shows SEM pictures of the various powders. Aluminium was used as the energetic fuel. Micrometer-sized tuber-shaped aluminium powder ( $<25 \mu\text{m}$ ) 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 of 100 nm to 200 nm. The nano-sized silicon powder ( $<50 \text{ nm}$ , purity  $>99\%$ ) was obtained from Hefei Kaier. Nano-sized CuO ( $<50 \text{ nm}$ ) and  $Bi_2O_3$  ( $<100 \text{ nm}$ , 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  $460 \text{ }^\circ\text{C}$  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- $K\alpha$  radiation ( $0.193609 \text{ nm}$ ) 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  $60 \text{ }^\circ\text{C}$ .

### 2.4. Thermal analysis

A Shimadzu DTA-50 instrument was used to perform thermal analysis. Alumina sample pans were employed and 5 mg  $\alpha\text{-Al}_2\text{O}_3$  was used as reference compound. Two thin copper discs ( $500 \mu\text{m}$  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

**Fig. 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.

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