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**Aluminium/Tin (IV) oxide thermite composite: Sensitivities
and reaction propagation**

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Abstract

Thermites are energetic composites made of metal and oxidizer particles that react according to an exothermic reaction and release large amounts of energy. Many possible metal and oxidizer couples exist in the literature. Here, the performance of the aluminium reducing metal and tin (IV) oxide (SnO_2) combination was reported as a function of the fuel/oxidizer mass ratio. The Al/ SnO_2 energetic composite, in stoichiometric conditions, was insensitive to impact, sensitive to friction and extremely sensitive to electrostatic discharge. The combustion velocity was determined to be close to 600 m/s. Changing the stoichiometry affected both the sensitivity thresholds to the friction test (160 N to > 360 N) and flame propagation velocity (480–588 m/s) of the Al/ SnO_2 composite. These results are reported for the first time.

Keywords: Nanothermites; SnO_2 ; Sensitivities; Combustion velocity.

1. Introduction

Within the energetic materials family, thermites are mixtures constituted of two main micron-scale components, a fuel metal and an oxidizer (metal oxide), reacting according to a redox reaction characterized by a high energy production (kJ/cm^3) coupled to extremely high flame temperatures ($> 2000 \text{ K}$) [1]. Fischer et al. listed various reacting pairs by varying either the metal (aluminium (Al), magnesium (Mg), zirconium (Zr) and bore (B)) and/or the metal oxide (iron (III) oxide (Fe_2O_3), molybdenum (VI) oxide (MoO_3), tungsten (VI) oxide (WO_3), copper (II) oxide (CuO), bismuth (III) oxide (Bi_2O_3)), demonstrating the possibility of tailoring the thermochemical proprieties of such energetic composites [1]. Over the past two decades, these energetic mixtures have attracted growing interest due to the use of nanopowders as alternatives to micron-sized reactants [2-4]. These new advanced nanocomposites, called metastable intermolecular composites (MICs) or nanothermites, exhibit improved energetic properties such as higher combustion velocities and reduced ignition delay times in a more homogeneous combustion mode, making them potential candidates as primers or pyrotechnic time delays.

Among the list of reacting pairs, $\text{Al}/\text{Fe}_2\text{O}_3$, Al/MoO_3 , Al/WO_3 and Al/CuO thermites seem to be the most investigated systems, probably because they exhibit high-energy properties [5-9; 10-14; 15-18; 19-24]. To the best of our knowledge, the aluminium-tin (IV) oxide (Al/SnO_2) energetic system has been poorly investigated compared with the above-mentioned ones and scant related information is available concerning the reactive behaviour, pressure released during the combustion and possible mechanism implied in the reaction (nature of the chemical species produced) [25-28]. Other work has focused on the use of tin (IV) oxide in energetic composites but rather as a third component at a low amount (additive, dopant) to control the reactivity of the investigated composite (Al/MnO_2) [29]. This existing situation is surprising because the thermochemical properties of the Al/SnO_2 energetic composite are quite interesting and demonstrate a performing system, similar to the Al/WO_3 energetic composite, with a heat of

reaction of 9.91 kJ/cm³ (2.88 kJ/g), an adiabatic reaction temperature of 2876 K and an amount of gas released of 0.34 g per 100 g of composite [1].

Herein, the detailed reactive behaviour, namely the sensitivity thresholds and combustion reaction speed, of the Al/SnO₂ thermite was investigated as a function of the fuel/oxidizer equivalence ratio within the composite. The results showed interesting and promising characteristics of the Al/SnO₂ energetic nanocomposite, equivalent to other classical nanothermites, with potential civil and military emerging applications.

2. Experimental section

2.1. Materials

Tin (IV) oxide material (SnO₂, < 10 μm, 99%) was purchased from Sigma Aldrich. Aluminium nanopowder (Al, Al-50P, 50 nm, 99%) and acetonitrile (CH₃CN, 99%) were obtained from Nanotechnologies Inc. and Prolabo, respectively. All chemicals were used without any further purification.

2.2. Preparation of the Al/SnO₂ thermites

The general combustion reaction of the Al/SnO₂ energetic system can be described as follows:

Typically, in pyrotechnics and thermite composites, the reactants are mixed according to a defined fuel/oxidizer weight ratio labelled the equivalence ratio (Φ). The corresponding formula is given in (2):

$$\Phi = \frac{\left(\frac{F}{O}\right)_{exp.}}{\left(\frac{F}{O}\right)_{st.}} \quad (2)$$

where F and O are the quantities of fuel (Al) and oxidizer (SnO₂) and the subscripts exp. and st. represent the experimental and stoichiometric values. For example, at the stoichiometry, the equivalence ratio takes the value of 0.239 for the considered energetic composite. Practically, note that a native alumina layer (Al₂O₃) surrounds the aluminium particles. The amount of

reactive aluminium in the commercial passivated aluminium powder (Al-50P) was determined to be equal to 52.2 wt.% using thermogravimetric analysis.

The Al/SnO₂ energetic composite was prepared as follows [17]. Briefly, considering an equivalence ratio of 1, 0.157 g of passivated-Al and 0.343 g of SnO₂ reactants were suspended in a round-bottomed flask containing 100 mL of acetonitrile. The solution was stirred for 1 hour interrupted by ultrasound periods (3 × 5 min.) to break agglomerates and obtain intimate mixing. Finally, the fuel/oxidizer mixture was recovered by evaporation of the solvent at 80 °C under vacuum (20 kPa) and was placed in an oven at 353 K for 4 hours.

The pyrotechnic behaviour (sensitivity, combustion velocity) of the Al/SnO₂ energetic composite was evaluated as function of the equivalence ratio varied between 0.8 – 1.8 (each 0.2).

2.3. Characterization techniques.

Tin (IV) oxide (SnO₂) and the Al/SnO₂ composite were characterized using standard laboratory characterization techniques. The crystallographic structure was verified by X-ray diffraction analysis achieved using a Bruker D8 Advance diffractometer (Cu K α radiation, $\lambda = 0.154026$ nm) equipped with a Lynxeye detector and working at 40 kV and 40 mA. The particle size distribution profile was examined by diffusion light scattering spectroscopy (DLS; Mastersizer 3000, Malvern Panalytical) on a SnO₂ particle aqueous suspension (0.1 g/L) and according to the Mie diffusion model. The morphology of the SnO₂ sample and Al-based composites were investigated by scanning electron microscopy performed on a FEI Nova NanoSEM 450 microscope operating at 10 kV. The energy dispersive X-ray spectroscopy (EDX) was used to establish an elemental mapping regarding the Al/SnO₂ energetic composite. The specific surface area of the SnO₂ material, relating to the Brunauer Emmet Teller model (BET), was determined by nitrogen adsorption measurements at 77 K using a Micromeritics ASAP2020 device. Prior to the measurement, the sample was degassed at 473 K for 6 hours.

The characteristics of the thermites, from a pyrotechnic point of view, were evaluated in terms of sensitivities (impact, friction and electrostatic discharge) and combustion velocity in a confined mode. Regarding the sensitivity tests, a detailed description of the different characterization techniques is given in [17]. Briefly, the mechanical sensitivity thresholds (impact and friction) of the energetic mixture were determined using a fall-hammer apparatus and a Julius Peter BAM device (Suceska 1992). The electrostatic discharge (ESD) sensitivity was measured using an ESD 2008 testing device from OZM Research s.r.o. The different reported sensitivity values represented the maximum stress for which no positive reaction was observed in six consecutive “no-go” tests. The probability of obtaining no combustion was 98.4% at the threshold value. The experiments were conducted in compliance with the standards established by NATO [30-32]. The combustion velocities of the thermites were determined, according a confined mode, from powdered Al/SnO₂ mixtures packed in cylindrical polymethylmethacrylate tubes (PMMA; diameter: 3 mm; length: 150 mm). The filling up was operated by successive controlled additions to preserve a constant loading density throughout the tube. A schematic illustration of the set-up is given in [17]. The combustion phenomena were recorded using a Photron FASTCAM high-speed camera (5×10⁴ frames/s) placed in front of the PMMA tube. The combustion speeds were determined using a series of three burn tests.

The bulk densities of the different energetic compositions were determined by the ratio of the amount of matter on the volume of the PMMA tube. Next, the bulk densities were expressed as a function of the theoretical maximum densities (TMD) of the considered mixture calculated from Eq. (3).

$$TMD = 1 / \sum_{i=1}^n \frac{m_i}{\rho_i} \quad (3)$$

where *i* is the considered chemical species and *m* and *ρ* are its mass and density, respectively. For example, considering the amount of Al (*ρ* = 2.70 g/cm³), Al₂O₃ (*ρ* = 3.05 g/cm³) and SnO₂ (*ρ* = 6.95 g/cm³) in a typical Al/SnO₂ thermite prepared with an equivalence ratio of 1, the TMD was determined to be equal to 4.794 g/cm³.

3. Results and Discussion

3.1. Characterizations of the SnO₂ oxidizer and Al/SnO₂ energetic composite.

Figure 1 shows the particle size distribution (PSD) and scanning electron microscopy (SEM) views of the SnO₂ material. The PSD of the tin (IV) oxide powder was found to match well with the manufacturer's data (Figure 1A). The powder presents a coarse PSD ranging from 1 to 10 μm with a shoulder in a size region of 0.3–1 μm . From the cumulative volume distribution curve, cumulative volume distributions (d_x with d as the average diameter of the particles or aggregates and x as the volume percent) can be determined. Thus, values of 1.59 ± 0.04 , 3.84 ± 0.06 and 8.40 ± 0.09 μm were found for the d_{10} , d_{50} and d_{90} of the SnO₂ powder, respectively. The microstructure of the SnO₂ powder is shown in Figure 1B. As clearly observed, the SEM views present a powder comprising highly agglomerated primary particles with a size located both at the nano- and submicron scales. The particle size was very large and covered a domain ranging from tens of nanometres (20–30 nm) to 200–300 nm for the largest particles. Careful observation of the SnO₂ powder failed to observe micron-sized primary particles, suggesting that the particle size distribution, described above (Figure 1A), reflected a high degree of agglomeration of the powder. Additionally, the specific surface area of the SnO₂ powder, by applying the BET model, was determined to be equal to 8 m²/g.

Figure 1: (A) Particle size distribution (PSD) curve and (B) SEM images of the SnO₂ material used as an oxidizer in the Al/SnO₂ energetic composites.

The aluminium/tin (IV) oxide energetic composite, prepared according to an equivalence ratio of 1, was characterized by SEM. A representative image is presented in Figure 2A. The energetic formulation comprised highly agglomerated nanoparticles in which the oxidizer and fuel cannot be easily distinguished because no distinct populations in term of the morphology and size were observed. However, the elemental mapping performed on the same domain at lower magnification (Figure 2B) revealed the presence of the aluminium (Al) and tin (Sn) metals on relatively all of

the observed domains. Thus, a homogeneous distribution of the fuel (Al) and oxidizer (SnO_2) in the as-prepared Al/ SnO_2 energetic thermite was expected.

Figure 2: SEM views of the Al/ SnO_2 thermite composite ($\phi = 1$) at (A) high magnification and (B) lower magnification with the corresponding elemental mapping where aluminium and tin are reported in green and blue plots, respectively.

The crystal structure of the Al/ SnO_2 composite was investigated using X-ray diffraction (Supporting Information 1). The diffractogram showed diffraction peaks that can be indexed to a tetragonal lattice associated with a $P4_2/\text{mm}$ space group describing the SnO_2 Cassiterite phase (JCPDS card 41-1445) and to a face-centred cubic structure with a $\text{Fm-}3\text{m}$ space group as expected for the aluminium phase (JCPDS card 65-2869). There are no other diffraction peaks confirming the amorphous character of the Al_2O_3 alumina layer covering the reactive aluminium.

Supporting Information 1: X-ray diffraction pattern of the Al/ SnO_2 thermite ($\phi = 1$) indexed with the SnO_2 (tetragonal lattice, $P4_2/\text{mm}$ space group) and Al (face-centred cubic structure; $\text{Fm-}3\text{m}$ space group) phases. The corresponding Miller planes were given.

3.2. Sensitivities of the Al/ SnO_2 thermite

The sensitivity level/threshold knowledge of the energetic materials and composites (thermites) is a key parameter for their future deployment both for civilian and military applications. Among the external stresses that can (accidentally) ignite the thermite mixtures, the mechanical and electrostatic ones are the most investigated. For example, in the case of mechanical solicitations, the ignition of energetic materials and thermite composites is commonly interpreted by the “hot spots” theory. This theory is based on the formation of local hot spots, having as origin interparticular friction, an adiabatic compression of gases or chemical decomposition, within the powder subjected to the considered stress [33]. When the hot spot temperature exceeds the decomposition/melting points of the components constituting the powder, the (accidental) initiation becomes.

The sensitivity test data for Al/SnO₂ with different fuel/oxidizer weight ratio energetic composites are presented in Table 1. Standards, either established by the United Nations intergovernmental organization and relating to the transport of dangerous goods or based on the literature, are given for comparison [34-36]. Note that the electrostatic discharge sensitivity standard given in the present work corresponds to the maximum energy that can be dissipated from a human being. First, compared with the standards, a lower sensitivity to mechanical stimuli such as friction stress and an extreme sensitivity to electrostatic discharge (≤ 0.21 mJ vs. 8.33–20 mJ) were noted for all the as-prepared Al/SnO₂ thermites. This behaviour is typical of fuel/oxidizer mixtures in particular regarding the ESD sensitivity [37].

Table 1: Sensitivity thresholds of the Al/SnO₂ thermite as a function of the fuel/oxidizer mass ratio (equivalence ratio ϕ).

Concerning the different Al/SnO₂ energetic composites, because the impact threshold was constantly superior to 49.6 mJ—i.e., the maximum value that can be determined from our fall-hammer apparatus—it is difficult to estimate a possible influence of the equivalence ratio. However, based on a previous study [30], all of the composites can be described as insensitive. Regarding the friction sensitivity, its threshold increases from 160 to > 360 N with the increase in the equivalence ratio from 0.8 to 1.8, allowing classification of the corresponding thermites as moderately sensitive to insensitive [31]. In scrutinizing the evolution of the sensitivity threshold, a “parabolic profile” seems to draw with a minima at 160 N for the Al/SnO₂ mixture compliant to the stoichiometry ($\phi = 1$). This minimum can be justified such that, in the whole volume of the thermite, at the micro- and nanoscale, the ideal chemical composition facilitating the initiation was observed. By varying the equivalence ratio (ϕ), SnO₂-rich ($\phi = 0.8$) and Al-rich ($\phi = 1.2$ to 1.8) energetic mixtures were elaborated and synonymous with a stoichiometry default between the Al and SnO₂ reactants for the energetic mixtures considered. Next, the probability of finding at any points of the energetic mixture the ideal chemical composition decreases. Accordingly, the

optimal conditions for the initiation are no longer met and it becomes necessary to provide a higher friction force (168 N, 216 N, 288 N, 324 N and > 360 N for $\phi = 0.8, 1.2, 1.4, 1.6$ and 1.8 , respectively) to create hot spots in the energetic composites to ignite them. Moreover, the force intensity was higher for Al-rich ($\phi = 1.2$ to 1.8) energetic mixtures because the increase in the aluminium amount equals the increase in the amount of alumina species within the mixture as Al nanoparticles are chemically composed of pure aluminium and alumina according to a core-shell structure (alumina surrounds the Al metal core). Alumina is a pyrotechnical inert material compared with tin (IV) oxide used initially as an oxidizer [1], explaining why the friction sensitivity thresholds for Al/SnO₂ are higher with ϕ superior or equal to 1.2 than for ϕ equal to 0.8 .

Concerning the electrostatic discharge sensitivity (ESD), the different Al/SnO₂ energetic composites (ϕ ranging from 0.8 to 1.8) exhibited a very high sensitivity to spark with values varying from 0.14 to 0.21 mJ, one order of magnitude lower than what a human body can dissipate (8.33 - 20 mJ). These very low thresholds are characteristic of extremely sensitive thermites for which an accidental reaction may occur during handling. As demonstrated by Weir et al. [38], one of the main points responsible for the ESD sensitivity is the aluminium fuel particle size. For example, considering Al/MoO₃ as an energetic composite, it was demonstrated that downsizing the Al particle size (from μm to nm) increases the electrical conductance of the mixture; accordingly, the minimum ignition energy is required for ESD ignition. This trend is supported by a spark energy density higher for small-particle-sized media that may easily lead to joule heating at the surface of the particles. This would lead to the formation of hot spots and trigger the initiation of the composite [38,39]. Thus, nanothermites are more sensitive to electrostatic discharge than their micron-sized counterparts. In the present work, all the investigated Al/SnO₂ mixtures were also exclusively made of nanosized Al particles, explaining the extreme sensitivity of the mixtures. By varying the equivalence ratio from 0.8 to 1.8 in the Al/SnO₂ composites, the mixture enriches itself in the conducting species (Al, electrical resistivity = $2.65 \cdot 10^{-8} \Omega/\text{m}$) and

impoverishes itself in the insulating species (SnO_2 , electrical resistivity = $3 \cdot 10^6 \, \Omega/\text{m}$). Thus, the conducting character of the energetic mixture is improved and better aligned with the above-mentioned principle. The increase in alumina (Al_2O_3 , electrical resistivity = $10^{12} \, \Omega/\text{m}$), as a protective layer of the aluminium particles, with an increase in the equivalence ratio, was noted by Weir et al. [38] as a benefit to the global conductivity of the mixture by producing more capacitive impedance.

3.3. Combustion velocity of the Al/SnO₂ thermite

The combustion velocities of the different Al/SnO₂ thermites by modifying the equivalence ratio ($\phi = 0.8$ to 1.8) were determined in a one-dimensional cylindrical design as described in section 2.3.

Before the burn experiment, the loading densities of the test tubes filled with the diverse Al/SnO₂ formulations were calculated. The average values of $0.422 \, \text{g}\cdot\text{cm}^{-3}$, $0.456 \, \text{g}\cdot\text{cm}^{-3}$, $0.431 \, \text{g}\cdot\text{cm}^{-3}$, $0.419 \, \text{g}\cdot\text{cm}^{-3}$, $0.415 \, \text{g}\cdot\text{cm}^{-3}$ and $0.416 \, \text{g}\cdot\text{cm}^{-3}$ were established based on a series of three tubes, determined for the Al/SnO₂ energetic formulation with an equivalence ratio ranging from 0.8 to 1.8 (every 0.2), respectively. The low standard deviations of the loading densities and linear regressions of the plots of the height filling as a function of the mass of matter added (Supporting Information 2) highlight a reliable and reproducible filling process. The loading densities correspond to $8.4 - 9.9\%$ of the respective theoretical maximum densities (TMD) of each formulation considered (Table 2). These data indicate that both the different energetic compositions can be characterized as being loose powders because of apparent densities lower than 10% of the TMD [40] and that a direct comparison of the combustion properties of the thermites can be performed because the gap between the percentages of TMD is negligible [41].

Figures 3 shows the sequences of combustion frames extracted from the video recordings of the combustions of the four energetic composites considered. The propagation of the combustion reaction in each system can be easily followed by the displacement of the luminous signal along the length of the tubes. All the Al/SnO₂ energetic composites behave similarly with a complete

and continuous combustion reaction on all the lengths of the burn experiment tubes; no premature extinctions were observed.

Supporting Information 2: Filling up height as a function of the mass added for (A) the thermite Al/SnO₂ ($\phi = 1$, series of 3 tubes) and for (B) all the Al/SnO₂ energetic composites (average filling up based on a series of 3 tubes for each composite). For clarity, the lines are plotted.

For all the Al/SnO₂ energetic composites, the first flame or spark within the tube was observed in the second image of the sequence considered, suggesting that a *globally similar* ignition delay time was recorded for all investigated compositions. However, for the very Al-rich mixtures ($\phi = 1.6$ and 1.8)—i.e., the energetic composites exhibiting a large deviation from the stoichiometric conditions defined by equation (1)—the propagation of the front flame was highly decreased in contrast to that of the other systems ($\phi = 0.8$ to 1.4). A delay of approximately $120\ \mu\text{s}$ was observed previously to observe the displacement of the luminous signal in the experiment tube. Thereafter, the burn rates progress normally within the thermite formulations. At this stage of the investigation, this behaviour was not well understood.

Figure 3: Sequences of the combustion images (top to down) of the Al/SnO₂ thermite with an equivalence ratio (ϕ) of (A) 0.8, (B) 1, (C) 1.2, (D) 1.4, (E) 1.6 and (F) 1.8. The interframe time was $60\ \mu\text{s}$, the scale bar reported in the inset of each first image represents 10 mm, and the vertical dotted lines delimit the tube extremities.

The residual chemicals collected at the end of the combustion tests were analysed using X-ray diffraction to determine the nature of the reaction products. The diffractogram is displayed in Figure 4. The diffraction peaks were attributed to the tin metal (Sn, JCPDS card 89-4898) and alumina ($\gamma\text{-Al}_2\text{O}_3$, JCPDS card 029-0063) phases described by a tetragonal and a cubic lattice, respectively. The presence of these compounds verifies the general combustion reaction of the Al/SnO₂ energetic system (1) and complements the work of Sullivan et al. who mentioned the release of oxygen (O₂) and tin (II) oxide (SnO) gaseous species during the combustion of the considered energetic mixture [27].

Figure 4: X-ray diffraction pattern of the reaction products of the Al/SnO₂ thermite system. (* glass threshold)

The combustion velocities of the energetic formulations were determined from the plot of the distance travelled as a function of the time and then performing a linear regression fit to these points (Figure 5). The initial and final extremities of the plots—i.e., the first 40 mm and last 20 mm with respect to the displacement (y axis)—were voluntarily discarded to eliminate possible artefacts or transient zones such as the acceleration phase and loss of confinement, respectively, thus allowing the acquisition of possible steady combustion velocities.

Figure 5: Front reaction position as a function of time elapsed for the Al/SnO₂ energetic composites (plot based on one burn tube experiment for each composite). For clarity, the lines are plotted.

Table 2: Combustion velocity of the Al/SnO₂ thermite as a function of the equivalence ratio (ϕ).

The combustion speeds of the different Al/SnO₂ energetic composites were determined and presented in Table 2. The combustion rates varied between 480 m/s and 588 m/s with an optimal propagation speed recorded when the energetic composite exhibited an equivalence ratio (ϕ) ranging from 1 and 1.4 to even 1.6. For fuel-lean Al/SnO₂ composites ($\phi = 0.8$), the propagation velocity was slightly delayed by 10%; however, for the highest fuel-rich formulation ($\phi = 1.8$), the burn rate value was reduced to more than 18%, establishing itself as the lowest combustion speed recorded.

One possible explanation for the higher combustion velocities of the slightly fuel-rich thermite mixtures ($\phi = 1$ to 1.4) may be the presence of the metal component (Al) in a significant amount. The metal, with good thermal properties, such as thermal conductivity and diffusivity, may promote a better heat transfer within the mixture, leading to enhanced combustion velocities [2]. For example, the thermal conductivities and diffusivity of Al are 236 W/m.K and $9.7 \cdot 10^{-5}$ m²/s, respectively, clearly higher than those of Al₂O₃ (36 W/m.K and $1.5 \cdot 10^{-7}$ m²/s, respectively) and

SnO₂ (40 W/m.K and $1.45 \cdot 10^{-7}$ m²/s, respectively) that comprise the composites [42,43]. However, when the amount of Al is very high in the thermite formulation ($\phi = 1.8$), the default oxidizer (SnO₂) amount is overpowered and becomes prejudicial to a quick reaction. By analogy, in the fuel-lean Al/SnO₂ thermite—i.e., $\phi = 0.8$ —the lack of metal fuel may support the low value of the burn rate (548 m/s).

Table 3 gathers the properties of some of thermites reactions mentioned in the literature such as Al/Fe₂O₃, Al/MoO₃, Al/WO₃, Al/CuO and Al/Bi₂O₃ [7,11,15,37,38,44-46]. Regarding the theoretical thermochemical data as the adiabatic reaction temperature and the heat of reaction, the Al/SnO₂ thermite exhibits rather low values compared to the other systems. For example, its adiabatic temperature and heat of reaction are of 2876 K and 15.39 kJ/cm³, respectively that is relatively far away the 3253 K and 20.82 kJ/cm³ for the Al/MoO₃ and Al/CuO composites, respectively. In term of gas releasing, the Al/SnO₂ reaction produces a significant amount of gas (0.29 mol./100 g of thermite), as the Al/CuO and Al/Bi₂O₃ formulations, which would make it interesting for applications where a mechanical work (transport, inflating) is needed such as in airbags or torch-type output. Then, from an experimental point of view, it is always difficult to compare performance (sensitivities, combustion velocity, and pressurization rate) of energetic systems between themselves (data against data). This is due to the fact that these data strongly depend on the physicochemical properties of the components constituting the systems considered (e.g., the morphology, granulometry, textural properties as well as the fuel/oxidizer equivalence ratio). However, the idea of *positioning* the Al/SnO₂ system among these counterparts remains interesting. Regarding the combustion speed, a value close to 600 m/s was determined for the Al/SnO₂ thermite which enters in the 550 – 950 m/s interval (Al/Fe₂O₃ – Al/MoO₃ nanothermites, respectively) characterizing the fastest combustion reaction velocities. Then, as advantages toward its counterparts, the Al/SnO₂ formulation is stand out by a high insensitivity to friction which could be benefit for transport operations. Lastly, the tin metal (Sn) produced by the

combustion reaction exhibits a low melting point (505.08 K), in opposite to the other metal products (iron, molybdenum, tungsten, copper), making the Al/SnO₂ formulation a potential candidate for nano-welding or short-circuit applications.

Table 3: Properties relating to thermite reactions. (a issued from [1], b determined in our laboratory but not yet published and c for not found in the literature). The combustion velocities were determined from burn experiments performed in a confined mode with hollow plastic tubes with an inner diameter of approximately 3 mm.

4. Conclusion

In this investigation, the performance of the Al/SnO₂ energetic formulation, in terms of sensitivity and reactive behaviour, has been described. The fuel:oxidizer weight ratio, or equivalence ratio (ϕ), was selected as the adjusting parameter. Globally, the energetic composite related to the stoichiometric ($\phi = 1$) is insensitive to shock (> 49.6 mJ), moderately sensitive to friction (160 N) and, classic for such composites, extremely sensitive to electrostatic discharge (0.21 mJ). The variation in the equivalence ratio, regardless of the trend (decrease or increase), does not modify the ESD and the impact sensitivities, while a mitigation of the friction sensitivity was recorded until the mixture was insensitive (> 360 N for $\phi = 1.8$). Such evolution was interpreted by the loss of the stoichiometry locally and the non-pyrotechnic character of the alumina (the amount increases with ϕ) in contrast to the SnO₂ oxidizer. The combustion speed of the powdered Al/SnO₂ mixture, in confined configuration (tubes), ranged from 480 to 588 m/s with the ceiling value within the 1- to 1.6-equivalence ratio domain.

These results showed that the Al/SnO₂ thermite, poorly investigated until now, exhibits energetic performances (sensitivities and combustion velocity) in the same order of magnitude as those of the most investigated energetic systems in the literature (Al/Fe₂O₃, Al/MoO₃, Al/WO₃, Al/CuO and Al/Bi₂O₃). Thus, this material can be considered an emerging solution in terms of energetic composites to help with successful deployment of thermites in many energetic applications.

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References

- [1] Fischer, S.H, M.C. Grubelich. 1998. *Theoretical energy release of thermites, intermetallics, and combustible metals*. Proceedings of the 24th International Pyrotechnics Seminar, pp 231-286, July 27-31, Monterey, USA.
- [2] Pantoya, M.L, J.J. Granier. 2005. *Combustion behaviour of highly energetic thermites: Nano versus Micron composites*. Propellants, Explosives, Pyrotechnics 30:53-61.
- [3] Valliapan, S, J. Swiatkiewicz, J.A Puszynski. 2005. *Reactivity of aluminum nanopowders with metal oxides*. Powder Technology 156:164-169.
- [4] Sun, J, M.L. Pantoya, S.L. Simon. 2005. *Combustion Behaviour of Highly Energetic Thermites: Nano versus Micron Composites*. Propellants, Explosives, Pyrotechnics 30(1):53-62.
- [5] Prakash, A, A.V. McCormick, M.R. Zachariah. 2004. *Aero-Sol-Gel synthesis of nanoporous iron-oxide particles: a potential oxidizer for nanoenergetic materials*. Chemistry of Materials 16:1466-1471.
- [6] Plantier, K.B, M.L. Pantoya, A.E. Gash. 2005. *Combustion wave speeds of nanocomposite Al/Fe₂O₃: the effects of Fe₂O₃ particle synthesis technique*. Combustion and Flame 140:299-309.
- [7] Bezmelnitsyn, A, R. Thiruvengadathan, S. Barizuddin, D. Tappmeyer, S. Apperson, K. Gangopadhyay, S. Gangopadhyay. 2010. *Modified Nanoenergetic Composites with Tunable Combustion Characteristics for Propellant Applications*. Propellants, Explosives, Pyrotechnics 35:384-394.
- [8] Zhang, W, B. Yin, R. Shen, J. Ye, J. Thomas, Y. Chao. 2013. *Significantly enhanced energy output from 3D ordered macroporous structured Fe₂O₃/Al nanothermite film*. ACS Applied Materials & Interfaces 5:239-42.
- [9] Hu, X, X. Liao, L. Xiao, X. Jian, W. Zhou. 2015. *High-Energy Pollen-Like Porous Fe₂O₃/Al Thermite: Synthesis and Properties*. Propellants, Explosives, Pyrotechnics 40(6):867-872.
- [10] Walter, K.C, D.R. Pesiri, D.E. Wilson. 2007. *Manufacturing and performance of nanometric Al/MoO₃ energetic materials*. Journal of Propulsion and Power 23(4):645-650.

- [11] Son, S.F., B.W. Asay, T.J. Foley, R.A. Yetter, M.H. Wu, G.A. Risha. 2007. *Combustion of nanoscale Al/MoO₃ thermite in microchannels*. Journal of Propulsion and Power 23(4):715–721.
- [12] Birce, D., M.L. Pantoya, V. Levitas. 2010. *The effect of preheating on flame propagation in nanocomposite thermites*. Combustion and Flame 157(8):1581–1585.
- [13] Clark, B.R., M.L. Pantoya, E.M. Hunt, T.J. Kelly, B.F. Allen, R.J. Heaps, M.A. Daniels. 2015. *Synthesis and characterization of flexible, free-standing, energetic thin films*. Surface and Coatings Technology 284:422-426.
- [14] Zakiyyan, N., A. Wang, R. Thiruvengadathan, C. Staley, J. Mathai, K. Gangopadhyay, M.R. Maschmann, S. Gangopadhyay. 2018. *Combustion of aluminum nanoparticles and exfoliated 2D molybdenum trioxide composites*. Combustion and Flame 187:1-10.
- [15] Sanders, V.E., B.W. Asay, T.J. Foley, B.C. Tappan, A.N. Pacheco, S.F. Son. 2007. *Reaction propagation of four nanoscale energetic composites (Al/MoO₃, Al/WO₃, Al/CuO and Bi₂O₃)*. Journal of Propulsion and Power 23:707-714.
- [16] Sullivan, K.T., W.A. Chiou, R. Fiore, M.R. Zachariah. 2010. *In situ microscopy of rapidly heated nano-Al and nano-Al/WO₃ thermites*. Applied Physics Letters 97:133104.
- [17] Gibot, P., A. Bach, L. Vidal, F. Schnell, R. Gadiou, D. Spitzer. 2017. *Safer and performing energetic materials based on polyaniline-doped nanocomposites*. Journal of Energetic Materials 35:136-147.
- [18] Comet, M., C. Martin, F. Schnell, D. Spitzer. 2017. *Nanothermite foams: From nanopowder to object*. Chemical Engineering Journal 316:807-812.
- [19] Petrantoni, M., C. Rossi, V. Conédéra, D. Bourrier, A. Pierre, C. Tenailleau. 2010. *Synthesis process of nanowired Al/CuO thermite*. Journal of Physics and Chemistry of Solids 71(2):80-83.
- [20] Zhou, X., R. Shen, Y. Ye, P. Zhu, Y. Hu, L. Wu. 2011. *Influence of Al/CuO reactive multilayer films additives on exploding foil initiator*. Journal of Applied Physics 110(9):094505.
- [21] Yan, S., G. Jian, M.R. Zachariah. 2012. *Electrospun nanofiber based thermite textiles and their reactive properties*. ACS Applied Materials & Interfaces 4(12):6432-6437.
- [22] Sullivan, K.T., J.D. Kuntz, A.E. Gash. 2012. *Electrophoretic deposition and mechanistic studies of nano-Al/CuO thermites*. Journal of Applied Physics 112(2):024316.
- [23] Sullivan, K.T., J.D. Kuntz, A.E. Gash. 2014. *The role of fuel particle size on flame propagation velocity in thermites with a nanoscale oxidizer*. Propellants, Explosives, Pyrotechnics 39:407-415.
- [24] McCollum, J., M.L. Pantoya, S.T. Iacono. 2015. *Activating aluminum reactivity with fluoropolymer coatings for improved energetic composite combustion*. ACS Applied Materials & Interfaces 7:18742-18749.
- [25] Ferguson, J.D., K.J. Buechler, A.W. Weimer, S.M. George. 2005. *SnO₂ atomic layer on ZrO₂ and Al nanoparticles: pathway to enhanced thermite materials*. Powder Technology 156:154-163.
- [26] Qin, L., T. Gong, H. Hao, K. Wang, H. Feng. 2013. *Core-shell structured nanothermites synthesized by atomic layer deposition*. Journal of Nanoparticles Research 15:2150-2165.
- [27] Sullivan, K., M.R. Zachariah. 2010. *Simultaneous pressure and optical measurements of nanoaluminium thermites: Investigating the reaction mechanism*. J. Propul. Power 26:467-472.

- [28] Wang, W, X. Song, W. Jiang, G. Deng, X. Guo, H. Liu, F. Li. 2011. Synthesis of nano-nickel coated micro-aluminium and thermal reactivity of aluminium/nickel stannic oxide thermite. *International Journal of Energetic Materials and Chemical Propulsion* 10(3):231–243.
- [29] Yang, Y., Z.C. Zhang, P.P. Wang, J.C. Zhang, F. Nosheen, J. Zhuang, X. Wang. 2013. *Hierarchical MnO₂/SnO₂ heterostructures for a novel free-standing ternary thermite membrane*. *Inorganic Chemistry* 52:9449-9455.
- [30] NATO. 1999. STANAG 4489. In: Standardization Agreement (STANAG) on Explosives, Impact Sensitivity Tests. NATO Standardization Agency: Brussels, Belgium.
- [31] NATO. 2002. STANAG 4487. In: Standardization Agreement (STANAG) on Explosives, Friction Sensitivity Tests. NATO Standardization Agency: Brussels, Belgium.
- [32] NATO. 2001. STANAG 4490. In: Standardization Agreement (STANAG) on Explosives, Electrostatic discharge Sensitivity Tests. NATO Standardization Agency: Brussels, Belgium.
- [33] Field, J.E, N.K. Bourne, S.J.P. Palmer, S.M. Walley. 1992. *Hot-spot ignition mechanisms for explosives and Propellants*. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences A* 339:269-283.
- [34] United Nations. 2007. Recommendations on the transport of dangerous goods: Manual of tests and criteria, 4th revised edition, New York and Geneva.
- [35] Greason, W.D. 2003. Electrostatic discharge characteristics for the human body and circuit pack, *Journal of Electrostatic*. 59:285–300.
- [36] Talawar, M.B., A.P. Agrawal, M. Anniyappan, D.S. Wani, M.K. Bansode, G.M. Gore. 2006. Primary explosives: Electrostatic discharge initiation, additive effect and its relation to thermal and explosive characteristics. *Journal of Hazardous Materials*. 137:1074–1078.
- [37] Puszynski, J.A., C. J. Bulian, J. J. Swiatkiewicz. 2007. *Processing and ignition characteristics of aluminium-bismuth trioxide nanothermite system*. *Journal of Propulsion and Power* 23(4):698-706.
- [38] Weir, C, M.L. Pantoya, M.A. Daniels. 2013. The role of aluminum particle size in electrostatic ignition sensitivity of composite energetic materials. *Combustion and Flame* 160:2279–2281.
- [39] Weir, C., M.L. Pantoya, G. Ramachandran, T. Dallas, D. Prentice, M. Daniels. 2013. Electrostatic discharge sensitivity and electrical conductivity of composite energetic materials. *Journal of Electrostatics* 71:77-83
- [40] Walters, K.C, D.R. Pesiri, D.E. Wilson. 2007. *Manufacturing and performance of nanometric Al/MoO₃ energetic materials*. *Journal of Propulsion and Power* 23:645-650.
- [41] Pantoya, M.L, V.I. Levitas, J.J. Granier, J.B. Henderson. 2009. *Effect of bulk density on reaction propagation in nanothermites and micron thermites*. *Journal of Propulsion and Power* 25:465-470.
- [42] Powell, R.W., C.Y. Ho, P.E. Liley, Thermal conductivity of selected materials, US Department of Commerce, Washington, 1966.
- [43] Turkes, P., Ch. Plunket, R. Helbig. 1980. *Thermal conductivity of SnO₂ single crystals*. *Journal of Physics C: Solid State Physics* 13:4941.

[44] Bach, A., P. Gibot, L. Vidal, R. Gadiou, D. Spitzer. 2015. *Modulation of the reactivity of a WO₃/Al energetic material with graphitized carbon black as additive*. Journal of Energetic Materials. 33(4):260-276.

[45] Foley, T., A. Pacheco. 2007. *Development of Nanothermite Composites with Variable Electrostatic Discharge Ignition Thresholds*. Propellants, Explosives, Pyrotechnics 32(6):431-434.

[46] Pichot, V., M. Comet M., J. Miesch J., D. Spitzer. 2015. *Nanodiamond for tuning the properties of energetic composites*. Journal of Hazardous Materials 300:194-201.

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Figure 1: (A) Particle size distribution (PSD) curve and (B) SEM images of the SnO₂ material used as an oxidizer in the Al/SnO₂ energetic composites.

120x89mm (150 x 150 DPI)

Figure 1: (A) Particle size distribution (PSD) curve and (B) SEM images of the SnO2 material used as an oxidizer in the Al/SnO2 energetic composites.

115x84mm (150 x 150 DPI)

Figure 2: SEM views of the Al/SnO₂ thermite composite ($\phi = 1$) at (A) high magnification and (B) lower magnification with the corresponding elemental mapping where aluminium and tin are reported in green and blue plots, respectively.

147x107mm (150 x 150 DPI)

Figure 2: SEM views of the Al/SnO₂ thermite composite ($\phi = 1$) at (A) high magnification and (B) lower magnification with the corresponding elemental mapping where aluminium and tin are reported in green and blue plots, respectively.

141x154mm (150 x 150 DPI)

Figure 3: Sequences of the combustion images (top to down) of the Al/SnO₂ thermite with an equivalence ratio (ϕ) of (A) 0.8, (B) 1, (C) 1.2, (D) 1.4, (E) 1.6 and (F) 1.8. The interframe time was 60 μ s, the scale bar reported in the inset of each first image represents 10 mm, and the vertical dotted lines delimit the tube extremities.

363x256mm (150 x 150 DPI)

Figure 4: X-ray diffraction pattern of the reaction products of the Al/SnO₂ thermite system. (*glass threshold)

186x160mm (150 x 150 DPI)

Figure 5: Front reaction position as a function of time elapsed for the Al/SnO₂ energetic composites (plot based on one burn tube experiment for each composite). For clarity, the lines are plotted.

197x162mm (150 x 150 DPI)

	Equivalence ratio (ϕ)	Impact (J)	Friction (N)	ESD (mJ)
Standards	/	2	80	8.33 - 20
Al/SnO ₂ _μm	0.8	> 49.6	168	< 0.21
	1	> 49.6	160	0.21
	1.2	> 49.6	216	0.14
	1.4	> 49.6	288	0.14
	1.6	> 49.6	324	< 0.14
	1.8	> 49.6	> 360	< 0.21

	Equivalence ratio (ϕ)	TMD (%)	Combustion velocity (m/s.)
Al/SnO ₂ _μm	0.8	8.4	548 ± 5
	1	9.5	581 ± 18
	1.2	9.4	588 ± 11
	1.4	9.4	579 ± 15
	1.6	9.6	566 ± 16
	1.8	9.9	480 ± 6

Energetic formulation (nm-reactants)	Adiabatic reaction temperature (K) ^a	Gas production (mol. gas / 100 g) ^a	Heat of reaction (-Q) ^a		Sensitivity			Combustion rate (m/s.) (% TMD)	References
			kJ/g	kJ/cm ³	Shock (J)	Friction (N)	ESD (mJ)		
Al/Fe ₂ O ₃	3135	0.14	3.95	16.51	/ ^c	/ ^c	1.25	550 (8)	[7] [37]
Al/MoO ₃	3253	0.24	4.70	17.90	/ ^c	/ ^c	0.05 - 0.25	950 (11)	[15] [37] [38]
Al/WO ₃	3253	0.14	2.91	15.90	> 49.6	8 - 144	< 0.14	925 (9)	[15] [17] [44]
Al/CuO	2843	0.54	4.07	20.82	> 49.6 ^b	9 ^b	< 0.14	802 (6)	[15] [45]
Al/Bi ₂ O ₃	3253	0.47	2.11	15.22	> 49.6	2	0.000125	646 (17)	[15] [46]
Al/SnO ₂	2876	0.29	2.87	15.39	> 49.6	216	0.14	588 (9)	This work

Supporting Information 1: X-ray diffraction pattern of the Al/SnO₂ thermite (□ = 1) indexed with the SnO₂ (tetragonal lattice, P42/mnm space group) and Al (face-centred cubic structure; Fm-3m space group) phases. The corresponding Miller planes were given.

140x120mm (150 x 150 DPI)

Supporting Information 2: Filling up height as a function of the mass added for (A) the thermite Al/SnO₂ ($\phi = 1$, series of 3 tubes) and for (B) all the Al/SnO₂ energetic composites (average filling up based on a series of 3 tubes for each composite). For clarity, the lines are plotted.

198x163mm (150 x 150 DPI)

Supporting Information 2: Filling up height as a function of the mass added for (A) the thermite Al/SnO₂ ($\phi = 1$, series of 3 tubes) and for (B) all the Al/SnO₂ energetic composites (average filling up based on a series of 3 tubes for each composite). For clarity, the lines are plotted.

198x162mm (150 x 150 DPI)