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# Mechanical desensitization of an Al/WO<sub>3</sub> nanothermite by means of carbonaceous coatings derived from carbohydrates

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13 Abstract: Nanothermites show great developmental promise in the near future in civilian, military 14 and aerospace applications due to their tuneable reactive properties (ignition delay time, 15 combustion velocity and pressure release). However, the high mechanical sensitivities of some of 16 these energetic nanocomposites can make transportation and handling them hazardous. Here, a 17 mechanical desensitization (shock and friction) of an Al/WO3 nanothermite is successfully obtained 18 by means of carbon adding through the pyrolysis of naturally occurring molecules (carbohydrates). 19 The combustion behaviour of the carbon-based energetic mixtures were also evaluated and a 20 respectable reactivity has been evidenced.

21 Keywords: Nanothermites; Saccharides; Carbon; Desensitization; Energetic nanocomposites.

## 23 1. Introduction

22

24 The mixtures of metal and oxide powders at the micro-scale, which are known as thermites, are 25 interesting energetic composites for specific applications, such as in the ordnance domain. The 26 reaction between both components is described as an exothermic oxidoreduction chemical reaction 27 leading to a high adiabatic temperature [1]. The amount of energy released during the reaction is 28 considerable and can reach, in some cases, 20 kJ/cm<sup>3</sup>. The adiabatic flame temperatures are also very 29 impressive with values ranging from 2000 to 3000 K. However, these traditional micro scale thermites 30 may suffer from low performance, such as poor reactivities, high ignition delay times and low 31 combustion velocities. These intrinsic reactive properties can be widely improved by the exclusive 32 use of nanosized metallic and oxides powders since the chemical reactions are governed by 33 diffusion/transport phenomena at the interphase of the reactants [2]. The shorter the diffusion 34 pathway is, the better the reactive properties. In such a configuration, the thermites, which are 35 referred to as nanothermites or metastable intermolecular composite (MIC) materials, attract much 36 attention [3-10]. These are very promising energetic composites and can advantageously substitute 37 for explosives in many pyrotechnic applications due to their high available energy densities and 38 reaction rates [11-13] while being free of highly toxic metal (mercury and lead) [11-13]. However, the 39 downside of obtaining such reactive properties is that, in most cases, the sensitivities of the thermites 40 to external stresses, such as mechanical ones, are highly increased [14]. In addition, the extreme 41 sensitivity of the nanothermites towards the electrostatic discharge does not need to be demonstrated. 42 Subsequently, such behaviors can be harmful to the expected potential applications of these kinds of 43 energetic composites since accidents can occur and the safety of the users cannot be assured. The 44 development of desensitized nanothermites that maintain suitable reactivity is thus of primary 45 importance. From an international point of view, the United Nations intergovernmental organization 46 has established standards for the transport of explosive goods [15]. The energetic materials are

- 47 classified with respect to their sensitivity thresholds relating to several stresses, such as impacts,
- 48 friction, electrostatic discharge, temperature increases, magnetic fields and so on. According to these
- 49 standards, the energetic compositions of the nanothermites are crucial to their future promise, as
- 50 expected.

51 In the literature, a number of investigations have been conducted on mitigating the sensitivities of 52 nanothermites. Aluminium metal was systematically chosen as the fuel and was mixed with different 53 oxide ceramics (CuO, WO<sub>3</sub>, MoO<sub>3</sub> and MnO<sub>2</sub>) [16-24] or a polymer (polytetrafluoroethylene, PTFE) 54 [25-27]. Desensitization can occur due to two different approaches: either by modifying the 55 aluminium particles (average particle size and passivizing alumina layer) [21,22] or by adding an 56 additive in the traditional binary fuel/oxidizer energetic composites [16-20,23-27]. Regarding this 57 second method, in a large majority of studies, synthetic carbons such as nanotubes, graphene and 58 nanofibres were selected that provided more efficient electrostatic discharge desensitization 59 [16,17,25-27,24] without effect or mention regarding the friction sensitivity. Now, some 60 nanothermites are very friction sensitive such as Al/CuO, Al/WO3 and Al/MnO2 with values of 61 ranged from 8 to 9 N [20, 24] that is widely below the 80 N standard required for the transportation 62 of energetic materials on public roads [15]. Maintaining such level of friction sensitivity could restrict 63 practical applications of nanothermites. Since then, the use of cheap amorphous carbon black (soot) 64 was proposed within the Al/WO<sub>3</sub> nanothermites to mitigate the friction sensitivity. Efficient 65 mechanical desensitization (impact and friction) was observed with low amounts of carbon additives 66 with a decreased combustion velocity [19]. More recently, two papers have shown the beneficial use 67 of non-carbonaceous additives to mitigate the sensitivities of nanothermites. The first one examined 68 and demonstrated the efficiency of a lubricating molybdenum sulphide material (MoS2) and 69 hexadecane (C16H34) as friction desensitizing additives in an Al/MoO3 nanothermite, but no reactive 70 properties were evaluated [23]. The second paper focused on the use of a polyaniline conducting 71 polymer in an Al/WO<sub>3</sub> nanothermite. The polymer proved to be a very promising additive for the 72 friction and electrostatic discharge desensitizations at low amounts (5 wt. %) while maintaining good 73 reactive performance for the investigated energetic formulation [20]. However, the performance of 74 the nanothermite strongly depends on the homogenization/dispersion of the additive within the 75 Al/WO<sub>3</sub> energetic composites.

Generally speaking, the adding of additives within nanothermites leads to a mitigated reactive behaviour of the considered energetic systems (decrease of the combustion velocity, longer ignition delay time...) that can thereby limit or divert the thermites of their initial practical applications but in other side, it is important to keep in mind that using nanothermites free of any additives stay extremely hazardous (handling and transportation). Definitively, the nanothermite desensitization is an emerging research topic where numerous aspects must be explored (additive nature, combustion behaviour and potential applications).

Here, a carbon coating onto the tungsten (VI) oxide nanoparticle surface as a method to mechanically desensitize an Al/WO<sup>3</sup> nanothermite is described. The carbon adding was achieved by a fast and simple process that carbonizes sucrose and cellulose molecules. These organic species (saccharides) are naturally occurring molecules, abundant and low cost, making them promising alternatives in the development of insensitive reactive energetic formulations. The performance of the nanothermites (mechanical sensitivities and reactivity), enriched or not enriched with carbon additives, were characterized.

- 90 2. Materials and Methods
- 91 Sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, reagent grade), acetonitrile (CH<sub>3</sub>CN, 99%) and tungsten (VI) oxide (WO<sub>3</sub>, 92 specific surface area (SSA) = 27 m<sup>2</sup>/g, 99.9%) were purchased from Sigma-Aldrich. Sulphuric acid 93 (H<sub>2</sub>SO<sub>4</sub>, 98%) was obtained from Carl Roth. Cellulose microcrystalline ((C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, reagent grade) was

provided by Alfa Aesar. Aluminium (Al, SSA = 37 m²/g, Al = 57.9 wt. %) nanopowder was purchased
 from NovaCentrix (United States). All chemical reagents were used as received.

#### 96 2.1. Tungsten (VI) oxide/carbon composites synthesis.

97 The weight percent of carbon additives in the WO<sub>3</sub>/C composite was fixed at approximately 3 wt. 98 % because, for lower values, tungsten (VI) oxide particle surfaces are not completely darkened, 99 especially with the use of a cellulose precursor. For that, the carbonization reactions of sucrose (Eq. (1)) 100 and cellulose (Eq. (2)) were considered.

$$C_{12}H_{22}O_{11}(s) \rightarrow 12C(s) + 11H_2O(g)$$
 (1)

101

$$(C_6H_{10}O_5)_n(s) \to 6nC(s) + 5nH_2O(g)$$
 (2)

105

106 The WO<sub>3</sub>/saccharide composites were assessed following two different approaches, depending on 107 the saccharide molecule (sucrose or cellulose) that was used as the carbon source. With the sucrose 108 molecule, the experimental approach can be described as follows. In a round-bottom flask (100 mL), 1 109 g of WO<sub>3</sub> and 0.19 g of sucrose were poured in 50 mL of demineralized water and stirred and 110 ultrasonicated for 30 min. Then, 100  $\mu$ L of concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) was added and the 111 stirring was maintained for 30 min. The round-bottom flask was placed on a rotating evaporator (100 112 rpm) and the liquid phase was evaporated at 90 °C under 200 mbar of pressure until a dry powder was 113 obtained. The product was heated up to 250 °C at 5 °C/min and maintained at this temperature for 2 114 hours to complete the drying. Concerning the preparation of the WO<sub>3</sub>/saccharide composites with the 115 use of cellulose as the carbon source, the experimental method is as follows. 1 g of WO<sub>3</sub> and 0.14 g of 116 microcrystalline cellulose were mixed in a mortar. Then, 100 mg of this mixture was inserted in a 5 mL 117 agate grinding jar that was equipped with an agate ball (5 mm, 100 mg) and placed on a mixer-mill 118 apparatus (Retsch MM200). The mixture was then milled for 5 min at a frequency of 25 Hz. The sucrose-119 based composite was not submitted to this post-treatment since sucrose has high solubility in water and 120 a high physical contact between components is expected after the solvent removal.

121 The resulting WO<sub>3</sub>/saccharide composites were heat-treated at 500 °C (5 °C/min., 2 hours) under 122 an argon flow (100 mL/min) in order to assess the WO<sub>3</sub>/carbon composites. This onset temperature was 123 chosen to be low in order to avoid interfacial reactions between the components leading to the synthesis 124 of the under- oxygenated tungsten oxides (WO<sub>3-x</sub>) or tungsten carbide (W<sub>x</sub>C) phases [28]. The 125 experimental yields in the solid carbon phase were close to 20 and 24 wt. % for the sucrose and cellulose, 126 respectively. These data are lower than the theoretical yields (42.1 and 44.5 wt. % according to Eq. (1) 127 and Eq. (2), respectively) mainly due to the formation of tars and gaseous carbonaceous species [29,30].

128 2.2. Nanothermite preparation.

129 The energetic formulations were prepared by mixing the tungsten (VI) oxide and aluminium 130 nanopowders in amounts defined according to the following stoichiometric chemical reaction (3).

$$2Al(s) + WO_3(s) \rightarrow Al_2O_3(s) + W(s)$$
 (3)

134 Therefore, an excess of aluminium was preferred in order to enhance the performance of the 135 nanothermites [4]. The excess active aluminium was adjusted by means of the equivalence ratio ( $\Phi$ ) 136 described in Eq. (4) and was fixed at a value of 1.4 instead of 1: 137

$$\Phi = ((F/O)exp.)/((F/O)st.)$$
 (4)

140 F/O is the mass ratio of fuel (Al) to oxidizer (WO<sub>3</sub>) and the subscripts exp. and st. stand for the 141 experimental and stoichiometric ratios, respectively.

138

139

The aluminium and the tungsten (VI) oxide powders, which were covered by carbon, were poured into 60 mL of acetonitrile, sonicated and stirred for 1 hour in order to break the aggregates and to prepare homogenous mixtures. The solvent was evaporated under 200 mbar of pressure at 80 °C until dry greyish powders were obtained. The powders were then placed in an oven at 80 °C for 4 hours. The energetic compositions were labelled as Al/WO<sub>3</sub>/C<sub>x</sub>, where x represents the nature of the biomolecules (*suc* for sucrose and *cell* for cellulose) that were used for the carbon adding within the nanothermite. An aluminotungstate nanothermite without a carbon additive was also prepared as a reference.

#### 150 2.3. Characterization techniques.

151 The chemical compositions (C and H) of the saccharide-derived carbon were performed by 152 burning at 1050 °C in a helium/oxygen flow with a Thermo Finnigan Flash EA 1112 apparatus. The 153 resulting gaseous products (CO2 and H2O) were separated on a chromatographic column and 154 quantified by using a thermal conductivity detector. The amount of oxygen was calculated with respect 155 to 100% of the material. The structures of the WO<sub>3</sub>/carbon composites were determined by using an X-156 ray Diffractometer (XRD, D8 Advance, Bruker) operating at 40 kV – 40 mA. The diffractograms were 157 collected in the 2 theta range  $10 - 80^\circ$  with a step size of  $0.02^\circ$  and a time by step of 0.1 sec. The weighted 158 amounts of carbon in the WO<sub>3</sub>/carbon composites were determined by thermogravimetric analysis 159 (SDT Q600 TA Instruments). The different composites were calcinated under air at between 25 - 800 °C 160 with a heating rate of 10 °C/min. A Scanning Electron Microscope (SEM, FEI Nova NanoSEM 450) 161 working at 10 kV was used to observe the morphology of the WO3/carbon samples that were previously 162 covered by a thin layer of gold (Desk II TSC Denton Vacuum).

163

164 The performance of the Al/WO<sub>3</sub>/C<sub>x</sub> nanothermites was evaluated at once in terms of the sensitivity 165 thresholds (impact and friction) and reactivity (combustion velocity). The impact sensitivity was 166 determined by a Julius Peters BAM Fall hammer apparatus and the threshold value is given in joules 167 (J). The friction sensitivity, whose value is in Newtons (N), was determined by a BAM friction 168 apparatus. More details on the working principles of these apparatuses are mentioned in [20]. The 169 different observed threshold values correspond to the highest value, for which 6 reaction tests are 170 related to a no-combustion result. The probability of obtaining no combustion at all is 98.4% at that 171 threshold value. All of the experiments were performed according to the standards that were 172 established by NATO [31-33]. Reactivity tests are performed on the nanothermite powders by means of 173 an optical flash ignition, which was inspired by the works of Wang et al. and Ohkura et al. [34,35]. The 174 energy density that was delivered by our laboratory-made equipment, which was equipped with a 175 xenon lamp, is 0.11 J/cm<sup>2</sup>. The heating temperature and the heating rate were determined to be higher 176 than 673 K and 5.10<sup>5</sup> K/sec., respectively, by means of a nanocalorimeter. Typically, 10 mg of powdered 177 energetic nanocomposites were placed on a glass substrate following a predefined contact surface of 178 approximately 50 mm2 in order to expose the same amount of matter to the flash. The glass substrate 179 was placed on the flash igniter device at a respective distance of 1 mm. All the combustion tests were 180 performed in air on all unconfined powdered Al/WO3 nanothermites (with or w/o the carbon additive). 181 The combustion phenomena of the energetic formulations were recorded by using a Photron

182 FASTCAM high-speed camera (10<sup>3</sup> frames/sec.) placed in front of the set-up.

#### 183 3. Results and Discussion

#### 184 3.1. Characterization of the saccharide-derived carbons and the WO<sub>3</sub>/C composites

Figure 1 (B and C) shows the X-ray diffraction patterns of the different WO<sub>3</sub>/carbon composites that were synthesized via pyrolysis at 500 °C of the corresponding WO<sub>3</sub>/saccharide multi-materials. The diffraction peaks that are observed for all composites, with respect to the examined angular domain, can be attributed to the WO<sub>3</sub> tungsten (VI) oxide phase (Figure 1A). The oxide ceramic crystallizes in the monoclinic structure with a P21/n space group, as reported in the crystallographic

190 card No 01-083-0950. Some of the Miller planes are given on the corresponding figure. No other

191 diffraction peaks are detected, thereby confirming the amorphous character of the carbon component

- 192 and the fact that the composites are free of any crystalline impurities such as tungsten carbide (WxC)
- 193 and oxygen-deficient tungsten oxides (WO<sub>3-x</sub>) phases. Absence of any amorphous phases was also
- 194 confirmed by Fourier Transform Infrared analysis (Figure S1).
- 195



196

197Figure 1: XRD patterns of the pure WO3 component (A) and the WO3/Csuc (B) and WO3/Ccell (C)198composites synthesized via the pyrolysis of the corresponding WO3/saccharide multi-materials.

199 The amounts of carbon in the WO<sub>3</sub>/carbon composites were determined by means of 200 thermogravimetric analyses, as reported in Figure 2. Two weight losses for the WO<sub>3</sub>/C<sub>suc</sub> and 201 WO<sub>3</sub>/C<sub>cell</sub> composites were recorded: below 300 °C and between 300 - 700 °C. While the first weight 202 loss can be attributed to the release of the adsorbed water molecules and embedded solvents on or 203 within the oxide/carbon composites, the second one is interpreted as the oxidation of the carbon-rich 204 phases. The weight losses at the highest temperature ranges are 3.5 and 3.1% for the WO<sub>3</sub>/C<sub>suc</sub> and 205 WO<sub>3</sub>/C<sub>cell</sub> composites, respectively.

206



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Figure 2: Thermogravimetric curves of the WO<sub>3</sub>/C<sub>suc</sub> and WO<sub>3</sub>/C<sub>cell</sub> composites under air between 25–
 800 °C.

To precisely characterize the oxide/carbon multi-materials, the chemical composition of the carbon phases were determined by elemental analysis. Table 1 gathers the data relating to the saccharide molecules after pyrolysis at 500 °C under argon for 2 hours. As reported, the resulting 213 products are mainly made of carbon with amounts that ranged from 86 to 82 wt. % with the use of 214 sucrose and cellulose as reactants, respectively. The presence of the hydrogen and oxygen 215 heteroatoms could be explained by the low temperature that was used for the pyrolysis, which causes 216 the incomplete carbonization of carbohydrates. In the literature, temperatures close to 900 °C are 217 classically used [28]. We voluntarily chose a lower pyrolysis temperature to avoid the formation of 218 tungsten derivatives (see Exp. Section - Paragraph 2.1), which could affect the combustion behaviour 219 of the energetic formulations that are investigated. To sum up, the WO<sub>3</sub>/C<sub>suc</sub> and WO<sub>3</sub>/C<sub>cell</sub> composites 220 are made of a carbonaceous phase that is globally similar in terms of its elemental composition with 221 an oxygen amount ranging from 11 to 15 wt. %, respectively, which is to the detriment of the carbon 222 amount.

- 223
- 224 225

226

**Table 1.** Chemical composition of the saccharide-derived carbon phases. The oxygen amount was calculated with respect to 100% of the material.

	C wt. %	H wt. %	O wt. %
Csuc	85.7	3.2	11.1
$C_{\text{cell}}$	82.0	3.3	14.7

227 The SEM images of the Tungsten (VI) oxide/carbon composites are presented in Figure 3. Both 228 composites, WO<sub>3</sub>/C<sub>suc</sub> (Figure 3A) and WO<sub>3</sub>/C<sub>cell</sub> (Figure 3B), are made of micron-sized particles with 229 surfaces that appear to be very rough. After careful observation, this roughness corresponds to the 230 highly agglomerated very small particles with very similar sizes to the pristine tungsten (VI) oxide 231 particles that are used for the WO<sub>3</sub>/carbon composites' preparation (Figure S2). The elemental 232 mappings of the carbon and tungsten chemical elements corresponding to these WO<sub>3</sub>/carbon 233 composites, which are established by means of energy dispersive X-ray (EDS) spectroscopy, are 234 presented in Figures 3A and 3B. Obviously, for both composites, the carbon and tungsten are evenly 235 distributed across all microparticles and seem to be intimately mixed. The fact that carbon and 236 tungsten can be observed at identical places suggests the successful coating of the carbon additive 237 onto the tungsten (VI) oxide particles' surface.

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This hypothesis was confirmed by means of transmission electron microscopic analysis, as shown in

Figure 4, where core-shell structures were observed for both WO<sub>3</sub>/carbon composites. However, the

carbon coating that was achieved from the sucrose precursor seems to be less uniform and

245 homogeneous on the WO<sub>3</sub> nanoparticles' surface (Figure 4A) where large carbonaceous matter was

- sometimes found between the tungsten-based particles rather than the carbon-shell of the cellulose
- 247 molecules (Figure 4B).
- 248



#### 249 250

**Figure 4:** TEM images of the (A) WO<sub>3</sub>/C<sub>suc</sub> and (B) WO<sub>3</sub>/C<sub>cell</sub> composites.

251 After mixing with the aluminium nanoparticles in order to prepare the nanothermites according 252 to the experimental section, the amounts of carbon were recalculated as 2.7 and 2.4 wt. % in the 253 Al/WO<sub>3</sub>/C<sub>suc</sub> and Al/WO<sub>3</sub>/C<sub>cell</sub> energetic formulations, respectively (2.3 and 2.0 wt. %, respectively, 254 when taking into account the alumina layer coating the aluminium nanoparticles). The 255 microstructures of both aluminotungstate energetic formulations were also examined by scanning 256 electron microscopy (SEM) and the corresponding images are shown in Figures 5A and 5B for the 257 nanothermites that are enriched with the carbonization products of sucrose and cellulose, 258 respectively. For both Al/WO<sub>3</sub>/C<sub>x</sub> mixtures, a similar result is obtained, namely, the observation of 259 very fine particles on all examined samples, and when larger particles are seen, they correspond to 260 an agglomeration of smaller ones, as previously observed for the WO<sub>3</sub>/carbon composites (Figure 3). 261 The aluminium nanoparticles seem to be well distributed within the two as-prepared nanothermites 262 without leading to microstructural evolutions. The microscopic views of the ternary energetic 263 systems are accompanied by the aluminium, carbon and tungsten elemental mappings (Figure 5 -264 down). In a general way, both composites exhibit effective and successful volume distributions for 265 their three chemical components (except for oxygen). For the tungsten element, some islets describing 266 slightly richer domains in the transition metal can nevertheless be observed. As this trend is observed 267 on the images describing the Al/WO<sub>3</sub>/C<sub>suc</sub> and the Al/WO<sub>3</sub>/C<sub>cell</sub> systems, both as-prepared 268 nanothermites can then be said to exhibit similar homogeneities.

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**Figure 5:** SEM views of the (A) Al/WO<sub>3</sub>/C<sub>suc</sub> and (B) Al/WO<sub>3</sub>/C<sub>cell</sub> mixtures. The elemental mapping analysis of the aluminium (red plot), carbon (yellow plot) and tungsten (blue plot) are reported for each diffused electron image.

The two Al/WO<sub>3</sub> nanothermite mixtures that were prepared with carbon additives were used in their powder forms in order to assess their performances, such as their sensitivity thresholds for mechanical solicitations and their combustive behaviours.

#### 277 3.2. Sensitivities of the Al/WO<sub>3</sub>/C nanothermites.

The mechanical sensitivities, i.e., impact and friction of the ternary energetic formulations are presented and compared to the binary Al/WO<sub>3</sub> nanothermite in Table 2. The different sensitivity thresholds were determined according to the protocol detailed in [20].

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Table 2. Mechanical (impact and friction) sensitivity thresholds for the Al/WO<sub>3</sub>/C nanothermites
 (weight % of carbon of approximately 2.7 and 2.4 from sucrose and cellulose as the carbon sources,
 respectively).

	Impact (J)	Friction (N)
Standards	2	80
Al/WO <sub>3</sub>	42.2	8
Al/WO <sub>3</sub> /C <sub>suc</sub>	> 49.6	216
Al/WO3/Ccell	47.1	324

285

Regarding the impact sensitivity, the aluminotungstate binary formulation can be considered to be insensitive with a threshold value of 42.2 N, which is significantly higher than the standard set at 2 J, as established by the United Nations [15]. The use of carbon as an additive leads to a systematic increase of this value with values of > 49.6 J and 47.1 J for the Al/WO<sub>3</sub> nanothermites that enriched with carbon coming from sucrose and cellulose carbonization, respectively. Thus, the adding of carbon within an Al/WO<sub>3</sub> energetic composite allows one to preserve and to strengthen the insensitivity of the formulation by increasing its impact sensitivity threshold [36].

Regarding the friction sensitivity, the Al/WO<sub>3</sub> nanothermite is very sensitive with a threshold value of 8 N compared with the standard value of 80 N established by NATO [15]. The use of carbon, regardless of its origin (sucrose or cellulose), allows one to definitely raise the sensitivity threshold value of the aluminotungstate nanothermite ranging from 216 N (carbon sucrose) to 324 N (carbon cellulose), which ranks the carbon-based ternary nanothermites as moderately sensitive [36].

298 In a general point of view, regarding the mechanical sensitivities, the very low impact and 299 friction sensitivities of the different Al/WO<sub>3</sub>/C<sub>x</sub> formulations might be explained by the fact that the 300 carbon adding, which leads to the preparation of either a core-shell structure and/or a homogeneous 301 mixture of tungsten (VI) oxide and carbon for the WO<sub>3</sub>/C<sub>cell</sub> and WO<sub>3</sub>/C<sub>suc</sub> composites, respectively 302 (Figures 3 and 4), allows one to isolate the oxidizer of the reducing metal compound. Consequently, 303 when the ternary energetic formulations are mechanically stressed (impact and friction tests), no hot 304 spots are generated at the aluminium tungsten trioxide interphase because no direct contact exists 305 between Al and WO<sub>3</sub>. The ignition of the thermites is then avoided at equivalent stress levels to the 306 ones that are defined for the binary reference Al/WO<sub>3</sub> nanothermite. Higher mechanical solicitations 307 are thus required to burn the carbon-based energetic compositions.

308 Compared to the literature dedicated to the desensitization of the nanothermites by means of 309 additives [16,17,19, 23-27], our results, which are focused on mechanical mitigation, can be compared 310 to only a couple of works [19,20,23,24] since most of them are focused on electrostatic mitigation. 311 Moreover, sometimes the nature of the oxidizer component used for the nanothermite formulation is 312 different (MoO<sub>3</sub>, MnO<sub>2</sub>...), which may lead to difficult direct comparisons [23,24]. However, due to 313 the necessity to compare our results to the literature, it can be argued that the present results, in a 314 general point of view, perform as well as or better than those in the literature. For instance, with 315 respect to the impact sensitivity threshold, Siegert et al. obtained desensitization ranging from 24.5 316 to 44.2 J with 29 to 37 wt. % of carbon nanofibres added (depending on the selected method for 317 introducing the additive within the Al/MnO2 nanothermite) [24], and Gibot et al. obtained a threshold 318 value of 20 J with the addition of the polyaniline conductive polymer (5 wt. % within the Al/WO3 319 energetic system) [20]. Thus, the present results are similar to the results that were obtained by Bach et al. with a 5 wt. % of carbon black as the desensitization agent in the Al/WO<sub>3</sub> nanothermites (impact sensitivity > 49.6 J) [19]. Regarding the friction sensitivity threshold values that were obtained in this work (216 and 324 N depending on the carbon source), again, the data are very competitive since they are clearly superior to the results of Kelly et al. (120 N with a 5 wt. % of MoS<sub>2</sub> as an additive within an Al/MoO<sub>3</sub> nanothermite) [23] and slightly lower and/or on the same order of magnitude as those of [19,20,24], namely, > 360 N, with an amount of additive that was almost twice as much as the present work.

327 3.3. Combustion of the Al/WO<sub>3</sub>/C nanothermites.

The combustion properties of the Al/WO<sub>3</sub>/carbon nanothermites with added carbon coming from sucrose or cellulose carbonization are compared with the classical Al/WO<sub>3</sub> nanothermite behaviour.

The camera flash ignition process has been carried out to investigate the combustion phenomena. The advantages of this method are that it does not depend on the environmental conditions (temperature, pressure, humidity...), it delivers constant thermal energy and it can be performed under air on unconfined powdered energetic systems. Then, all phenomena related to the evolution of the gas through carbon combustion should be avoided. Some selected video images of the combustion of the three investigated energetic nanocomposites are shown in Figure 6.

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**Figure 6:** Sequences of the combustion images of the (A) Al/WO<sub>3</sub>, (B) Al/WO<sub>3</sub>/C<sub>suc</sub> and (C) Al/WO<sub>3</sub>/C<sub>cell</sub> nanothermites. The first image of each series corresponds to the ignition of the energetic powders. The elapsed time between pictures is 200 µsec.

342 In all cases, the energetic compositions completely combusted because no residual solid 343 products (traces) were found on the glass substrate at the end of the tests. An intense white light is 344 observed in the first frames of the recording videos and it takes on a yellow-orange tone at the end 345 of the combustion, expressing a rapid increase in the temperature followed by cooling. This result 346 suggests that the addition of a carbonaceous agent does not lead to a total loss of reactivity for the 347 Al/WO3 nanothermite. Nevertheless, while a clapping sound was heard for the Al/WO3 348 nanothermite, the combustions of the carbon-doped systems are quieter. Most likely, the latter have 349 a less powerful energetic character than the binary energetic nanocomposite. This mitigation of the 350 combustion energy might be due to the energy consumed by the carbon additive for its own 351 combustion (Eq. (5)), leading to a slight decrease of the total released energy according to the 352 examined formulations.

- 353 354
- 355

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$
 (5)

This trend is expected and has been already noted with the adding of other additives within a binary nanothermite [19,20]. Finally, when observing the different sequences of the combustion images of 358 the Al/WO<sub>3</sub>, Al/WO<sub>3</sub>/C<sub>suc</sub> and Al/WO<sub>3</sub>/C<sub>cell</sub> nanothermites (Figure 6), it might be that the combustion 359 velocity is higher for the binary energetic system (Figure 6A) than for the ternary ones (Figures 6B 360 and C). This hypothesis is based on the fact that for equivalent amounts of energetic matters (w or 361 w/o carbon) that are ignited by means of an optical flash, the yellow-orange colour (synonymous 362 with the cooling step of the energetic formulation) of the incandescent cloud located above the glass 363 substrate is visible at a shorter duration time (~ 0.8 msec.) of the combustion of the binary Al/WO<sub>3</sub> 364 nanothermite than for the carbon-enriched Al/WO<sub>3</sub> nanothermites ( $\geq$  1.2 msec.). In other words, for 365 the same amount of matter, the total combustion of the undoped mixtures is quicker than that for 366 carbon-doped ones. To the same extent, the combustion velocities of both Al/WO<sub>3</sub>/carbon ternary 367 nanothermites seem to be relatively similar. However, no more accurate details of the combustion 368 velocity can be provided since it is difficult to evaluate the covered distance by the reaction front as 369 a function of time. Currently, a reflection is conducted to optimize the in-air-combustion tests 370 (without the confinement of nanothermites) and permit an accurate characterization of the 371 combustion velocities of these carbon-doped energetic formulations.

#### 372 4. Conclusions

373 In summary, an efficient friction desensitization of an Al/WO<sub>3</sub> nanothermite while maintaining 374 acceptable reactive properties was achieved using carbon as a desensitizing agent. The carbon 375 additive was obtained by carbonizing the sucrose and cellulose molecules, which are naturally 376 occurring molecules, abundant and low cost. With a carbon amount slightly lower than 3 wt. % 377 within the nanothermite (with the carbon coming from the sucrose carbonization), the mechanical 378 sensitivity threshold values are about >360 N and >49.6 J for the friction and impact tests, respectively, 379 which are at least 4.5 and 25 times higher than the international standard values (80 N and 2 J, 380 respectively). With regard to the reactive properties (ignition and combustion velocity), the carbon-381 doped Al/WO<sub>3</sub> nanothermites exhibit slightly mitigated properties compared to the Al/WO<sub>3</sub> binary 382 counterpart. Finally, this approach may be seen as providing the beginnings of an answer to the 383 development of safer reactive nanothermites.

- Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: FTIR spectra
   of the different WO<sub>3</sub>/C composites. The pristine WO<sub>3</sub> material is also reported. Figure S2: SEM view of the
   pristine WO<sub>3</sub> material.
- 387 Author Contributions: P.G. suggested and guided this research, and wrote the paper. Q.M, A.B. and P.G. carried 388 out the experimental work including materials syntheses, the diverse characterizations (TGA, XRD, sensitivities 389 and combustion tests) and the corresponding data interpretation. F.S. performed the electron microscopy 390 coupled to the energy-dispersive X-ray spectroscopy. R.G. and D.S. supervised closely the study, the 391 interpretation of data and helped in the proofreading of the manuscript.
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