

Nanothermites: A short Review. Factsheet for Experimenters, Present and Future Challenges

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Abstract: Nanothermites are the most important family of energetic materials in contemporary pyrotechnics. This article traces the main research which was carried out in this still recent domain and the challenges that remain to be overcome. The academic effort of past two decades has brought nanothermites from the status of laboratory curiosities to the one of pre-industrial materials. Different aspects of nanothermites are discussed in order to provide valuable information to scientists experimenting in this domain. Experimental details on the preparation and the disposal of nanothermites are reported. The current research

on nanothermites deals with: (i) the development of new aluminothermic mixtures; (ii) the preparation of hybrid compositions by combining nanothermites with explosive nanopowders and (iii) the study of reactive properties. From an academic standpoint, the future challenges are to find new compositions and effects. From a practical standpoint, the effort must focus on the integration of nanothermites and their derivatives in pyrotechnic systems. Toxicological concerns are expected to become increasingly important over the next decade.

Keywords: Nanothermites · aluminum nanopowder · aluminothermy · explosives · energetic materials.

1 Introduction

Nanothermites are the most promising family of energetic compositions: These deflagrating materials will play a central role in the modernization of science in pyrotechnics and will lead to cutting-edge developments and applications in this domain.

A thermite is a composition, which comprises of an oxygen donor, such as a metallic oxide or salt, and of an oxygen acceptor, which is a reducing metal or metalloid. Nanothermites are prepared from fine powders, whose particle size generally ranges from nanometer to sub-micrometer scale.

With the benefit of hindsight of two decades of research in this domain, aluminum nanopowder has proven to be some of the best, if not the best fuel for nanothermites. The commercial availability of stable aluminum nanopowders, with narrow particle size distribution and well defined metal/oxide content, has boosted the research in this field. Numerous aluminothermic nano-compositions, prepared from metal oxides or oxygenated metallic salts, have been studied over the last few years in several laboratories around the world and the outstanding reactivity of these energetic materials is now being better understood. However, the complexity of nanothermites is such that a lot of research is still necessary to integrate these new substances into pyrotechnic systems, in order to make best use of their exceptional performances and versatility.

One of the most promising ways for current and future research in the domain of nanothermites is to combine these energetic compositions with organic explosive nano-

powders, in order to obtain hybrid nanocomposites materials. These “post-pyrotechnics” are the missing link between the domains of pyrotechnics and explosives.

This article aims at showing the evolution of research in the domain of nanothermites, from the beginning to present-day. This analysis intends to infer trends from the most significant results published in this research area, and to identify the future challenges that must be overcome to integrate nanothermites into pyrotechnic systems. To this end, a lot of academic research remains to be done, that will lead to numerous great findings.

2 What are the Fuels for Nanothermites?

A look to Mendeleev's periodic table shows that the number of elements which can be used as fuels in nanopowders is actually quite limited. The most promising metallic fuels were identified by Fischer and Grubelich, who calculated the thermochemical performances of a series of thermites prepared from these substances [1]. The heats released by the oxidation of these fuels into their stable oxides were used to determine a criterion of interest, which is the square root of the product of oxidation heats by weight and by volume (Table 1). The geometric mean of both

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Table 1. Critical review of fuels of potential interest for preparing nanothermites.

Fuels	Oxides	Q_{exp} (kJ.g^{-1}) [1]	Q_{exp} (kJ.cm^{-3}) [1]	Criterion of interest ($\text{kJ.g}^{1/2}.\text{cm}^{-3/2}$)	Drawbacks
Al	Al_2O_3	31.1	83.8	51.0	–
B	B_2O_3	59.0	138.0	90.2	Reactive only at high temperatures
Be	BeO	67.6	125.1	92.0	Highly toxic, carcinogen (category 1)
Hf	HfO_2	6.4	85.3	23.4	Difficult to prepare at nanoscale
La	La_2O_3	6.5	39.7	16.0	Not stable
Li	Li_2O	43.1	23.0	31.5	Not stable
Mg	MgO	24.8	43.1	32.7	Not stable
Nd	Nd_2O_3	6.3	43.9	16.6	Not stable, ignition at low temperature
P (red)	P_4O_{10}	23.8	51.3	34.9	–
Si	SiO_2	32.4	75.5	49.5	Reactive only at high temperatures or with strong oxidizers
Ta	Ta_2O_5	5.7	92.7	22.9	Very expensive
Th	ThO_2	5.3	61.8	18.1	Radioactive
Ti	TiO_2	19.7	88.9	41.9	Ignition at low temperature
Y	Y_2O_3	10.7	47.9	22.7	–
Zn	ZnO	5.4	38.3	14.3	Not stable
Zr	ZrO_2	12.1	78.7	30.8	Difficult to prepare at nanoscale

quantities gives a better estimation of the intrinsic interest of fuels and allows classifying them more objectively than by considering separately their two oxidation heats. The reason for this relies in the fact that the fuels used for preparing energetic nanomaterials are in the state of nanopowders; their density in the composition depends of different parameters such as the size and the morphology of the particles of the mixture components, but also of the packing density of the material. The use of the oxidation heat by weight is therefore more intuitive even though, the final amount of heat released depends on the mass of fuel present in the volume occupied by the composition. The criterion of interest presented in table 1 reflects these both aspects. On the basis of these purely thermochemical considerations the best fuels for nanothermites should be beryllium, boron, aluminum and titanium. The high toxicity

and the carcinogenicity of beryllium compounds preclude the use of this metal in nanothermites, particularly given that reaction products would be dispersed in form of fumes made of fine particles. Boron nanopowder can be used as fuel for nanothermites, but the reactivity of these compositions is disappointing in comparison to what is expected of such materials, when considering theoretical properties of boron. According to Yeh and Kuo, the combustion of micrometer-sized boron particles (2–3 μm) in a flame occurs in two continuous stages. The first step is the burning of the boron particle which is still covered with its oxide layer. This step lasts until molten $(\text{BO})_n$ phase, which first forms on the surface of boron particles by the reaction between B_2O_3 and B upon heating, has been totally vaporized and the boron core had reached its melting temperature (2450 K). The second step is the fully-fledged combustion of bare boron. This



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phenomenon is either controlled by oxygen diffusion or by chemical kinetics. The first mechanism is observed for large boron particles, under high pressure, while the second mechanism concerns small particles burning under small pressure [2]. Young *et al.* have studied the combustion of primary boron nanoparticles aggregated in clusters with sub-micrometer sizes. They showed that the combustion of boron nanoparticles also occurs in two stages, like that of coarser boron particles. The ignition time of boron nanoparticles decreases with increasing temperature, but the concentration in oxygen of the atmosphere in which they are ignited has low incidence on this parameter. Conversely, the oxygen concentration has a significant effect on the combustion of boron nanoparticles, which is more pronounced at the lower flame temperatures. Young *et al.* have also observed that the combustion time of boron nanoparticles is neither limited by diffusion nor by chemical kinetics. This result led them to conclude that the dissipation of heat by sub-micrometer sized boron particles makes melting of boron more difficult and requires that the combustion be carried out at a higher flame temperature [3]. The full efficiency of boron nanopowder is reached when it is used in energetic compositions with flame temperature high enough to evaporate the oxide layer and melt the boron core. For instance, Sullivan *et al.* have shown that the addition of boron nanopowder, with average primary particle diameter of 62 nm, enhances the reactivity of an Al/CuO nanothermite [4]. Titanium nanopowder has particularly low ignition temperature (100–200 °C), which makes it unsafe to handle in large amounts. Finally, aluminum is the fuel which has the most of desirable properties for being used in nanothermites: Al nanopowders give very reactive compositions with many oxidizers, they are stable once they have been accurately passivated, they have relatively low toxicity and are now prepared at industrial scale in relatively large amounts.

Amongst the other fuels proposed by Fischer and Grubelich, zirconium and hafnium are likely to be difficult to prepare in nanopowders, owing to their particularly high boiling points. Most of other metals are not stable enough to be prepared in nanopowders, or to be kept in this state. The long-term stability of a metal powder essentially depends on the physicochemical properties of the oxide layer which forms on the surface of the particles. If it is porous to oxidizing species or if it delaminates from the metal, the corrosion is permanent. The ratio metal/oxide then decreases along time, and the heat released by the oxidation can sometimes cause the spontaneous ignition of the powder. The problem of pyrophoricity is more marked for a metal nanopowder because, on the one hand, the large surface area of nanoparticles accelerates the heat release and, on the other hand, the low thermal conductivity of the powder limits heat dissipation, which induces temperature rise in the sample. To minimize the ignition hazards of unstable metal nanopowders, it is recommended to keep them in small samples, typically no more than some grams,

and to avoid exposure to oxidizing atmospheres. The use of metallic containers, which favors heat dissipation and prevents the buildup of electrostatic charging, is advised. The volume of the container must be defined to maximize the loading density, i.e. to minimize the amount of oxidizing species in contact with the metal nanopowder.

Interestingly, Fischer's classification does not report the use of zinc as potential fuel for thermites. This is probably due to the fact that this metal has thermochemical properties of little interest for this purpose. However, the low boiling point of zinc (B.P: 907 °C) makes it easy to evaporate and to prepare at nanoscale. From an experimental standpoint, zinc reacts weakly with oxides such as CuO or Bi₂O₃ which, however, strongly react with aluminum. This behavior could be explained by the fact that zinc vapor reacts on the surface of these oxides. The ZnO shell produced by the reaction subsequently limits the diffusion of Zn vapor to unreacted oxide core, which inhibits the reaction. On another note, zinc sub-micrometer sized particles are very sensitive to ageing in contact with atmosphere. The observation of a commercial Zn "nanopowder" stored in a plugged glass bottle thirty months apart, revealed a marked ageing of the sample. Zinc particles initially have a round shape, with facets. In the aged material, small ZnO particles have grown on the surface of the zinc sub-micrometer sized particles, which have lost their well defined shape and agglomerated in large clusters (Figure 1).

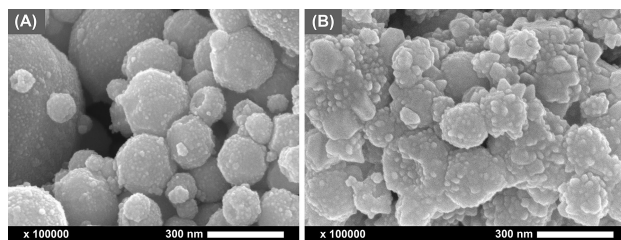


Figure 1. SEM pictures of a sub-micrometer sized Zn powder at bottle opening (A) and thirty months after (B).

Silicon and red phosphorus are metalloids of interest for preparing nanothermites, which are not mentioned in Fischer's classification. Porous silicon mixed with strong oxidizing salts, such as metallic perchlorates, gives fast-deflagrating compositions [5–7]. Strictly speaking, these energetic materials cannot be considered as thermites, because they contain low amounts of metal that does not directly participate to the pyrotechnic reaction. It seems that silicon, just like boron, should rather be considered as an additive to improve the reactivity of the aluminothermic compositions than as a pure fuel for the nanothermites [5]. Red phosphorus [8] mixed with metallic oxides gives combustible compositions [9] with interesting properties [10]. The use of sub-micrometer sized particles of red phosphorus could increase the reaction of these compositions.

To conclude, an ideal fuel for nanothermites is a stable, non-toxic powder, composed of sub-micrometer sized or nanosized particles, with the highest possible oxidation heat, which reacts strongly in a temperature range extending from 500 °C to 1000 °C. On that basis, aluminum is by far the best fuel for preparing nanothermites.

3 Aluminum Nanopowder: A key Material for Nanothermites

The history of thermites is closely tied to the one of aluminum. The widespread availability of this metal, whose industrial production was a major scientific and engineering challenge of the nineteenth century, has led to the development of aluminothermic compositions by Goldschmidt, who patented their use for preparing metals, metalloids and alloys in 1895 [11]. Micrometer-sized thermites were mainly used for civilian purposes, such as rail welding or the shearing of steel structures. Military applications of these materials were limited to incendiary charges and flash compositions for flares. The intense research carried out in the past two decades on the processes for preparing at industrial scale aluminum nanopowders has led to commercial products (50–200 nm). As a consequence, the research on nanothermites has considerably grown in recent years.

3.1 On the Properties of Aluminum Nanopowders

The manufacturing of aluminum nanopowders is a technology difficult to master involving four typical steps: (i) the evaporation of aluminum; (ii) the condensation of the metal vapor in droplets with nanometric dimensions; (iii) the stabilization of Al nanoparticles by a thin oxide shell; and (iv) the passivation of the nanopowder by further oxidation. The preparation processes of aluminum nanopowders essentially differ by the technique used to evaporate aluminum. For instance, the metallic vapor can be produced by the electric explosion of wire, or by resistive heating, or by means of a plasma torch [12–16]. The ideal thickness of the alumina shell which covers the aluminum core is between 3 to 5 nm. Such samples are stable along time, provided that they are not exposed to moisture. Conversely, thinner oxide films (< 2 nm) lead to unstable powders which can be pyrophoric. The risk of spontaneous ignition exists in oxidizing atmospheres. It increases with the size of samples, due to the confinement of heat by aluminum nanopowder which is an insulating material at macroscopic scale [17]. It goes without saying that nanothermites must always be prepared from aluminum nanopowders which have been correctly passivated. The thickness measurement of the alumina shell can be performed by transmission electron microscopy on individual particles. An alternative method, which was proposed by Pesiri *et al.* for this purpose, is based on the determination of the Al/Al₂O₃ ratio by ther-

mogravimetric analysis (TGA) and the measurement of the BET specific area by nitrogen adsorption [14]. This method cannot be applied to characterize aluminum powders with micrometer-sized or large sub-micrometer sized particles, because the total oxidation of the metal core is difficult to achieve.

In aluminum nanoparticles, the oxide shell is amorphous and its density is about 3.2 g/cm³ [14]. The Al/Al₂O₃ ratio of an aluminum nanopowder decreases with its mean particle size. From a pyrotechnic point of view, the active part is unoxidized aluminum, which means that Al nanoparticles used to prepare nanothermites should not be too small. On the other hand, aluminum particles should not be too large, in order to keep the specific benefits of their small size. In practical terms, the most suitable Al nanopowders for manufacturing nanothermites have typical grain sizes between 50 to 120 nm.

The controlled formation of an alumina shell on the surface of Al nanoparticles is by far the most efficient method to provide an efficient and long-term stabilization of the material against oxidation. All other passivation methods, such as the coating of aluminum core by organic or inorganic substances are doomed to failure, because the metal reacts with the coating, which leads to the formation of impurities and to uncontrolled oxidation. For instance, Kwon *et al.* have observed that the passivation of aluminum nanoparticles by oleic or stearic acids resulted in the carbidization of the surface of particles along time. They also found that nitrocellulose-coated aluminum nanoparticles were strongly oxidized after one year ageing [18]. Jouet *et al.* have grafted perfluoroalkyl carboxylic acids on bare aluminum nanoparticles formed in situ by the catalytic reduction of aluminum hydride, but their aluminum content was extremely low [19]. Wang *et al.* have used an original process for coating aluminum nanoparticles by polytetrafluoroethylene in a controlled way. The PTFE film deposited on the surface of aluminum nanoparticles makes them hydrophobic, improves their resistance to moisture and slows down their dissolution in an alkaline solution [20]. Kaplowitz *et al.* have tried to stabilize aluminum nanoparticles by a shell of magnetite (Fe₃O₄) in order to have a reactive iron oxide layer instead of an inert alumina layer. Unfortunately, they observed that a thick alumina shell was forming at the interface Al/Fe₃O₄. In this material, the aluminum core is oxidized by the iron oxide, which in turn reacts with oxygen from the atmosphere until the alumina layer becomes thick enough to stop oxygen diffusion [21].

The alumina is rightly considered as an inert mass, which is responsible for the relatively low combustion heat of aluminum nanopowders (10–25 kJ/g) compared to the one of pure aluminum (31 kJ/g) [22]. However, mixtures made from aluminum nanopowder stand out from energetic compositions, which are prepared from other nanosized fuels. The reaction of nano-sized aluminothermic mixtures gives particularly strong combustions, which are not detonations [23], but that still propagate at high velocities

(0.1 to 2.5 km/s) [24]. The particular behavior of nano-Al based compositions could arise from the explosion of the core-shell structure of the aluminum nanoparticle upon ultrafast heating. This mechanism, which was called “melt dispersion mechanism” (MDM), was proposed by Levitas et al. in 2006 [25,26]. Despite numerous controversies, this mechanochemical approach seems to fit particularly well with experimental observations carried out on large nanothermite samples. To conclude, the oxide shell on aluminum nanoparticles should be seen as a “necessary evil”, as it all at once contributes to decrease the exothermicity and to improve the reactivity of aluminothermic mixtures.

The combustion of aluminum nanopowders is activated by a low energy input, delivered as high power impulses. For instance, the combustion of nano-Al with atmospheric oxygen can be triggered by an electrostatic discharge or by the light of a photographic flash, both providing very fast heating. The progressive heating of nano-Al powders under oxidizing atmosphere, leads to the slow oxidation of aluminum nanoparticles, which starts around 400 °C. The oxidation occurs in several steps: Al is first oxidized in solid state. In a second time, the metal melts (~650 °C) and the related change of density breaks the alumina shell. Liquid Al migrates to the surface where it is instantly oxidized [27]. The healing of cracks in the oxide shell slows the oxidation kinetics. However, when temperature is raised to higher levels (~1100 °C) the whole metal is finally oxidized. The full oxidation of aluminum core at such temperatures can be achieved only with nanopowders. Note that the color of the Al sample gives a good qualitative indication of whether the metal has been totally oxidized (or not) in the sample. An immaculate white sample only contains alumina, while even slightly grey coloration denotes the presence of unoxidized aluminum.

One of the most classical properties of nanomaterials is the depression of their melting point, which is shifted to lower temperatures. This effect increases in inverse function of the size of particles. As on one hand aluminum nanopowders used for preparing nanothermites are made of relatively large particles (> 50 nm), and on the other hand the pressure exerted by the oxide shell on the Al core tends to shift melting temperature to higher values, the melting point depression is not strongly marked in Al nanopowders.

3.2 On the Safe Handling of Aluminum Nanopowders

Precautions should be taken to handle aluminum nanopowders, for which the two main hazards are of toxicological and pyrotechnic natures. Although these aspects are particularly important, they are almost never addressed in literature.

Aluminum nanopowders do not have acute toxicity, but recent research has pointed out the role of aluminum in human auto-immune and neurodegenerative pathologies [28]. Scientists experimenting with nanoscale aluminum should

not lose sight of the long-term toxic effects of this metal. The most important portal of entry for nanoparticles in the body is respiratory tracts, because the skin efficiently protects the body against the penetration of nanoparticles that come in contact with epidermis.

The use of gloves for handling nano-Al is not recommended, especially with Pyrex glassware, because electrostatic charging disperses the powder, making it difficult to use cleanly and causing pollution of laboratory bench and atmosphere. Surfaces contaminated by Al nanopowder can be cleaned with wet absorbent paper towels in the presence of a surfactant to remove most of nanoparticles. Aluminum nanoparticles are easily trapped in the porosity of objects, either on surfaces or in the bulk. The example of a sponge used to remove nano-Al powder gives a good illustration of this problem (Figure 2). The washing of the sponge with water is carried out by twenty successive impregnation and spinning cycles. Although the sponge remains permanently soiled by the nanopowder, the washing in the presence of a surfactant makes it possible to eliminate most of the material trapped in the porosity. Liquid detergents must be systematically used to clean objects that have been in contact with nano-Al.

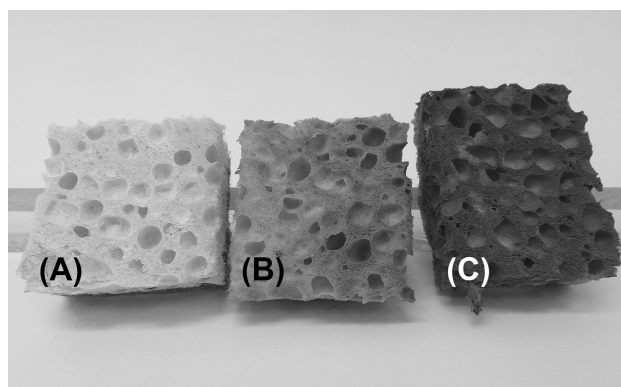


Figure 2. Aspects of sponge pieces which were: Simply soaked with water (A); first used to clean Al nanopowder and subsequently washed: In the presence of a detergent (B); with water only (C).

If aluminum nanopowder is accidentally spilled on hand skin, it must never be rubbed with a towel, because this would cause the nanoparticles to penetrate into the pores of the skin. The best cleaning technique is first to remove the nanopowder by gently shaking under an extractor hood, before careful washing residual contamination with liquid soap and cold water.

Aluminum nanopowders are composed of independent nanoparticles, which agglomerate in micrometer-sized clusters by surface forces. This morphology suggests that only a small part of the material can be dispersed if the material is handled with care. Nevertheless, it is highly recommended to work under an efficient extractor hood, in order to limit

the exposition to free Al nanoparticles. In an aerosol, fine particles follow the direction in which the air flow moves, even though each individual particle has an erratic trajectory. As an added precaution, respiratory protection equipment should be used, such as half-mask with FFP3 filters. It can be noticed that nanoparticles are smaller than the porosity of filtering cartridges and could theoretically pass through these systems. However, thank to the thickness of filters and to the ability of nanoparticles to stick on surfaces, most of them can be stopped. The highest degree of security is guaranteed by working in a glove box, which prevents any dispersion of the aluminum nanopowder in the atmosphere. This *modus operandi* is particularly recommended to handle large samples.

From a pyrotechnical point of view, aluminum nanopowder is a fuel, whose combustion is only possible in the presence of oxidizing species. Aluminum is more hazardous to handle in state of nanopowders, as it ignites easier and reacts faster than in micrometer-sized powders. Special care must be taken to avoid forming nano-Al/air aerosols, in order to avoid dust explosion.

Aluminum nanopowder reacts with practically all oxygen-containing chemicals. For instance, the mixtures of nano-Al with liquid or frozen water are combustible; such compositions were called ALICE (Aluminum-Ice) propellants and have been even used in experimental rocket motors by Risha *et al.* [29] Aluminum nanopowders also react violently with mineral acids. For instance, the pastes which are prepared from nano-Al and sulfuric acid, give hydrogen detonations when they are placed in an open flame [30]. The exothermicity of the reaction of nano-Al powder with orthophosphoric acid solutions can be tamed by the dilution with water of H_3PO_4 . Conversely, when the acid is dried with phosphorus anhydride, the heat released by the reaction ignites the mixture and leads to a hydrogen explosion [31]. The aluminum nanopowder reacts strongly with hydrochloric acid solutions. In a first step, there is an induction time resulting from the migration of the acidic solution to the aluminum core. In a second step, a runaway is observed owing to the sudden boiling of the solution. The temperature of the medium is raised by the heat released by the oxidation of aluminum. It leads to a decrease of the solubility of hydrogen chloride and to its fast degassing from the solution. The partial evaporation of water and the release of hydrogen, which occur at the same time, enhance the violence of the reaction. This mixture gives pneumatic explosions under confining due to the large amounts of gaseous species, which are quickly released. The subsequent explosion of the hydrogen may occur in the presence of an ignition source, but the presence of incombustible gases (H_2O vapor, HCl) makes it more difficult to activate than for pure hydrogen. In conclusion, the contact of aluminum nanopowder with acidic solutions should be avoided, except for specific research and in small amounts. These mixtures are more hazardous than those

prepared from micrometer-sized aluminum powders, and should be handled with care.

The reaction of aluminum nanopowders with alkaline solutions of sodium or potassium hydroxides, also releases hydrogen. The induction time is relatively short; the corrosion is accelerated by the rise of temperature. In the presence of excess hydroxide, aluminum is totally dissolved as aluminate ions. This reaction can be used to neutralize most of nanothermite compositions, by reactive dissolution of the fuel. This protocol must be used with caution, to avoid the formation of an explosive atmosphere with the hydrogen released, for instance by working under a well ventilated extraction hood. The nanothermite should be added by small fractions in the solution, and by waiting between each addition that the reaction reaches completion, before adding the next amount. Moreover, this neutralization protocol must never be used for compositions that release oxygen in the contact with alkaline solutions, such as mixtures containing persulfates [32].

Aluminum nanopowders can be easily ignited by low energy and high power inputs, such as those supplied by an electrostatic discharge or a photographic flash [33]. The temperature light impulse delivered by a flash can reach several hundred of degree Celsius, with a heating rate of about one million degrees per second. This mode of ignition is not specific to aluminum: Combustible nanopowders with dark color in loose powder state, such as carbon nanotubes, boron or titanium can be ignited in this way. This also applies to energetic compositions which contained these materials. The effect of the flash on nanopowders originates from their insulating properties: The heat absorbed on the surface hardly diffuses in the bulk, leading to the ignition of the powder. The intensity of the heat flux, which is delivered by a photographic flash, decreases proportional to the square of the distance between the sample and the bulb, but the use of flashes to photograph samples of aluminum containing nanopowders is however dis-
advised.

4 Nano-Aluminothermic Mixtures: Preparation and Disposal

In the classical meaning, thermites are mixtures of aluminum powder with metallic oxides. This definition should be extended to every mixture, in which atoms with high electronegativity (O, S, F...) are exchanged between an oxidizer and a fuel, which also contain a significant amount of metallic elements. For instance, Bi_2O_3/B or CuO/P mixtures can be considered as thermites, while $KClO_4/Si$ or KNO_3/B compositions do not fit this definition.

Nano-aluminothermic mixtures are thermite compositions, in which aluminum and often the oxidizer are nanopowders. The oxidizer can be a metallic oxide [24,34–37], or an oxygenated salt such as: permanganate [38,39], perchlo-

Table 2. Most representative solvents used for preparing nanothermites.

Solvent	Boiling point (°C) [49]	Dipolar moment (D) [50]	Main drawbacks	Ref.
Diethyl ether	34.5	1.14	Formation of explosive organic peroxides	[51]
Petroleum ether	42–62	~0	Poor dispersing properties	[52]
Acetone	56	2.70	–	[53]
Hexane	68.7	0.00	Poor dispersing properties	[54–56]
Acetonitrile	81.6	3.90	Toxicity	[57, 58]
2-Propanol	82.3	1.65	Can react with aluminum	[59–61]
Water	100	1.86	React with aluminum / Additives are needed	[62]
Dimethylformamide	153	3.81	High toxicity and high boiling point	[63]

rate [40, 41], periodate [42], sulfate [43], peroxodisulfate [44] or even phosphate [31].

Nano-aluminothermic mixtures are sometimes mixed with nanopowders of organic energetic materials, such as high explosives (RDX, PETN, HMX, CL-20...), in order to form hybrid compositions whose reactive features are inbetween those of pure nanothermites and pure explosives.

In this part, the most representative preparation techniques of these materials will be described, with focus on their advantages and their limits. The goal is to provide benchmarks, in the light of experimental observations made in our laboratory, as well as information drawn from the analysis of published research in this field.

4.1 Dry Mixing

Dry mixing is the technique used to prepare classical micro-meter-sized thermites, which have low sensitivity to any kind of stresses. For nanothermites, this technique should be reserved to the preparation of mixtures which are particularly insensitive to friction or, that contain one component which can be altered in the contact of a liquid. For instance, metallic sulfates can be mixed with aluminum nanopowder by grinding in a mortar [43]. In first place, this procedure is justified by the insensitivity to friction of these energetic compositions. By the way, sulfates can dissolve or lose their crystallization water in some solvents.

This mixing technique is also recommended for the preparation of composite materials, which contain additives whose nanostructuring can be altered in the contact of liquids. A first example is provided by the detonating compositions prepared from nanothermites and explosive nanopowders [45]. In this case, the mixing must be necessarily performed without liquid, in order to avoid the dissolution/recrystallization phenomena which would lead to particle coarsening. A second example comes from Pichot *et al.*, who have prepared Al/Bi₂O₃ compositions, from bismuth oxide which was preliminarily coated by detonation nanodiamonds (Bi₂O₃@DND) [46]. In this case, the mixing of the modified oxide with aluminum nanopowder cannot be made in a liquid, which would lead to the separation of DND coating from Bi₂O₃.

The dry mixing of sensitive compositions must be performed with extreme caution, always on small samples, typically 0.01 to 1 gram, depending on the nature of the material prepared. The best way to carry out the mixing is first to crush the sample between two smooth surfaces, to make the phases interpenetrate; then to break the soft agglomerates [47] with the edge of a spatula. This protocol needs to be repeated several times, to homogenize the composition. A good indicator is given by the homogeneity of the color of the powder, when it sheared on the surface on which the mix is realized [48].

In the specific case of experiments that do not require compositions with a good homogeneity, the mixing can be done by simple agitation in a vortex mixer or in a Turbula shaker-mixer. Very sensitive compositions can even be prepared by this method, because the lack of homogeneity makes them far less sensitive than those that would be prepared from the same components by a technique leading to a better homogeneity.

4.2 Mixing in Liquids

The most common method for preparing nanothermites is to disperse the components in a liquid by ultrasonic agitation, vibration or magnetic stirring and then to remove the solvent by evaporation under reduced pressure or by drying for several hours in a laboratory oven. The underlying concept of the mixing in liquids is to cancel the surface forces responsible for the aggregation of nanoparticles, in order to separate and to mix them as homogeneously as possible. In this regard, the choice of the mixing liquid is also essential. The dispersive medium should have several properties: (i) low boiling point for fast evaporation; (ii) acceptable dispersing properties; (iii) good compatibility with the phases dispersed; (iv) adequate chemical stability and (v) ideally low toxicity.

The liquid used for preparing a nanothermite should be chosen wisely by considering the nature of its components. The main liquids which are classically used for this purpose are shown in table 2. The best dispersing liquids are acetonitrile, dimethylformamide (DMF) and acetone, which have the highest dipolar moments. Alkanes are a poor choice from this point of view, but on the other hand, they are

chemically inert towards nanothermite components. The solvents that contain functional groups may cause the corrosion of aluminum. For instance, aluminum is oxidized by alcohols at their ebullition temperature, in the absence of water traces [64]. The chemical equilibrium of the oxidation is shifted by the formation of the alkoxide, which is dissolved in parent alcohol. The corrosion of aluminum by acetone is extremely slow (from 0.03 to less than 0.5 mm/year [65]) and is insignificant for bulk metallic pieces. In the case of aluminum nanopowder, this effect cannot be neglected, as this corrosion rate corresponds to 0.06 nm/min to 1 nm/min and could lead to a substantial degradation of the material. The effects of corrosion are probably enhanced by the sonication treatments frequently used to improve the mixing. In conclusion, the time of contact with the dispersing liquid must be minimized, both in the mixing step and the subsequent drying of the sample.

For optimizing the mixing of the nanothermite components in a liquid, the slurry is stirred either by a mechanical stirring or, in most cases, by ultrasounds. The sonication can be applied with an ultrasonic bath or with a sonicating horn. The differences between these two techniques rely in the density of power delivered to the sample. In the bath, the density of energy brought to the sample is less important, because the energy carried by the sonic waves is dispersed in a large volume and must pass through the glass wall of the round-bottomed flask which contains the slurry. With the sonicating horn, the sonic waves are directly applied to the sample, which allows one to more efficiently break agglomerates and mix nanoparticles. In turn, the sample can be polluted by the particles produced by the cavitation erosion of the metallic horn. Another important point is to optimize the sonication duration, in order to insure the homogenization of the mixture without altering the physicochemical properties of nanopowders.

The analysis of articles dealing with nanothermites shows that many researchers dry the nanothermite suspensions by natural evaporation of the liquid in air [66–70]. This method is not recommended, as in these conditions, the nanoparticles have time to organize in a non-random, albeit uncontrolled manner. This reflects the broader principle that the preparation of nanomaterials needs short times for limiting the formation of a long-range order, not only at molecular level but also at particle scale. In practice, nanothermite slurries must be dried as fast as possible, in non static conditions, *e.g.* by using an experimental device like a rotary evaporator. The drying must be brought to completion, in order to remove the solvent adsorbed in the porosity of the material. The presence of residual solvent increases the sensitivity thresholds and changes the reactivity of the nanothermite. In addition, the thermal decomposition of some solvents can produce toxic compounds, such as hydrogen cyanide in the case of acetonitrile.

The last step is the recovery of the sample, which is formed of large nanothermite agglomerates. Some authors use sieves for breaking these agglomerates and for obtain-

ing a powder with a better defined macroscopic grain size. This last step is hazardous, especially with nanothermites which are very sensitive to friction [71]. The careful crushing of large agglomerates with a spatula seems a better option for this purpose, because nanothermites are less sensitive to compression than to friction. In other words, internal friction of agglomerates and particles are to be preferred to friction of the composition against external objects.

4.3 Resonant Acoustic Mixing (RAM)

Resonant acoustic mixing is an elegant technology, which was developed over the past decade for preparing homogeneous solid/solid, solid/liquid and liquid/liquid formulations for various applications. The principle is based on the interaction of low frequency acoustic waves (58–65 Hz) with the material mixed, which induces strong accelerations of the particles up to one hundred times gravitational force [72].

The use of RAM was introduced by Nellums *et al.* for preparing Al/Bi₂O₃ ultrasensitive compositions [71]. More recently, Sullivan *et al.* have prepared Al/CuO thermites by acoustic mixing, from nano-sized copper oxide and aluminum powders (0.08–108 μ m). According to these authors, RAM is more appropriate than ultrasonication for mixing a nanopowder with a micrometer-sized powder, to avoid the segregation of the components [73]. On the other hand, Hope *et al.* have obtained explosive core-shell particles or co-crystals by this technique. They have also shown that the heat generated by internal frictional strengths in the samples during a RAM cycle causes a rise of temperature. The temperature reaches a plateau at 50 °C for powdered materials or 80–90 °C for a viscous polymer. Such heating level is compatible with the mixing of most energetic materials, including nanothermites and even organic explosives [74].

RAM seems to be a good technique for preparing relatively large samples of nanothermites or energetic nanocomposite materials, in a simple and fast way. This does not negate the pyrotechnic hazard inherent in the preparation of nanothermites and their derivatives. Extreme caution is necessary when using RAM, because this technique requires relatively important amounts of energetic material for operating well.

4.4 Disposal of Nano-Sized Aluminothermic Mixtures

The method for disposing of nanothermites consists to separate the aluminum from the oxidizer. Despite its apparent simplicity, this method is difficult to achieve experimentally. The separation of homogeneous mixtures of nano-sized components cannot be performed easily by a physical process. This is why another process must be considered for this purpose. The most efficient technique relies in the oxidation of the aluminum part in the aluminothermic composition.

This operation is carried out in aqueous alkaline solutions of sodium or potassium hydroxides, present in large excess compared to the amount of aluminum which must be oxidized. This chemical disposal process ensures the complete neutralization of pyrotechnic properties, insofar as aluminum totally loses its ability to fuel the aluminothermy reaction. The main hazard of this reaction is related to the fast release of hydrogen (Figure 3), owing to the particularly low flammability and explosive limits of this gas [75]. From a practical point of view, the solution used to neutralize the nanothermite is poured into a beaker, so that to have sufficient space to allow expansion of the foam formed by the hydrogen bubbles. The solution is continuously stirred to improve the contact of the powder with the solution and also to break the foam. The nanothermite must be added by small portions into the solution, in order to minimize the release of hydrogen and the foaming. It is necessary to wait the resorption of the foam, before adding a new portion of nanothermite. Indeed, the foam hinders the contact of the material with the solution, which can lead to a runaway of the reaction if a second sample is added prematurely.

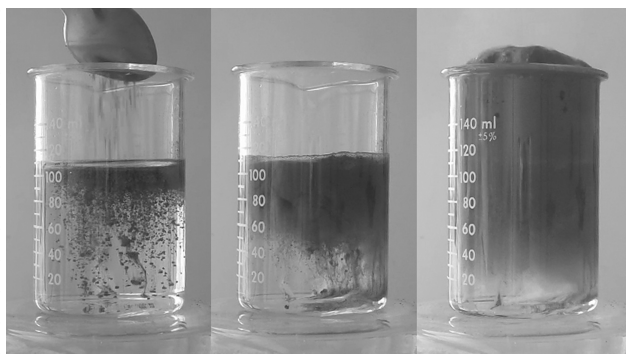


Figure 3. Oxidation of aluminum nanopowder in an aqueous solution of potassium hydroxide.

The neutralization of hybrid energetic nanocomposite materials is a three-step process. In a first time, the material is dispersed in a liquid which dissolves the explosive part. In a second time, the nanothermite is separated from the liquid by filtration or centrifugation. The final step consists in the neutralization of the nanothermite by the method described above and the disposal of the explosive solution.

5 Current Challenges

The research carried out in the domain of nanothermites during the first decade of this century has mainly focused on the study of compositions based on metal oxides. The most representative metallic oxides which have been used for preparing nanothermites in powder form are: Ag_2O , Bi_2O_3 , Cr_2O_3 , CuO , Fe_2O_3 , MnO_2 , MoO_3 , NiO , SnO_2 , TiO_2 , WO_3

[17]. The violence of the combustion depends on the amount of gases released by the reaction, but also on the size and the morphology of oxide and aluminum particles and on the degree of homogeneity of mixtures. Compositions prepared from Bi_2O_3 or CuO are extremely reactive and their combustion in small amounts (~ 10 mg) gives an explosion, which is similar (albeit less intense) to the one produced by the detonation of primary explosives like lead azide or silver acetylide. This effect shows that the combustion propagates at a supersonic velocity in these compositions. Conversely, the mixtures prepared from refractory oxides such as Cr_2O_3 or TiO_2 produce no gas when they burn and their combustion is slow. Other mixtures have intermediate burning behavior. The propagation velocity of the flame front in nanothermites confined in tubes is most often between 0.1 and 1 km/s. The highest flame propagation velocity (~ 2.5 km/s) was obtained by Martirosyan with an $\text{Al/Bi}_2\text{O}_3$ nanothermite [76]. According to Sullivan *et al.*, most of nanothermites prepared from metallic oxides ignite above the melting temperature of aluminum, with the exception of the $\text{Al/Bi}_2\text{O}_3$ composition whose ignition temperature is below this point [77]. The ignition of nanothermites prepared from metallic oxides, is sometimes activated by the oxygen released by the decomposition of oxide (CuO ; Fe_2O_3); it can also occur before the oxygen release (Bi_2O_3 ; SnO_2) or still without oxygen release (MoO_3 ; WO_3) [78]. For these last two kinds of nanothermites, the ignition is initiated by the interfacial contact between the metallic oxide and aluminum nanoparticles. The reactive sintering of nanoparticles is an important phenomenon which was evidenced by Sullivan *et al.* on Al/CuO and Al/WO_3 nanothermites. Upon fast heating, aggregated CuO nanoparticles undergo fast melting and coalescence. This effect is increased when oxide nanoparticles are closely mixed with aluminum nanoparticles, owing to the exothermicity of the reaction between the both components. The calculated timescale of sintering of CuO nanoparticle is comparable to the characteristic reaction timescale. This observation led Sullivan *et al.* to conclude that sintering processes could play an important role in the reactivity of nanothermites [77].

In the state of loose powder, nanothermites burn actually faster than any other micrometer-sized pyrotechnic composition, but they do not detonate and have lower flame propagation velocity (FPV) than explosives [23]. The main challenge is to increase their reactivity, either by playing on the nature of the oxidizer or by adding energetic gas generating substances. The understanding of the underlying mechanisms is of prime importance, to find new ways for enhancing the reactivity. These aspects should be studied by keeping in mind that reactivity must be always put first, while however not neglecting the problem of sensitivity.

5.1 Research of new Nanothermite Compositions

The research of new nanothermite compositions should consider the oxidizers used in conventional micrometer-sized pyrotechnic mixtures, including chlorates, perchlorates, bromates, iodates, periodates, peroxides, permanganates, nitrates, sulfates and persulfates. These oxidizing substances can be used either as micrometer-sized or as nano-sized powders with aluminum nanopowder.

The research of new aluminothermic nanostructured compositions must be guided by the idea to increase the amount of gases released by the reaction, in order to have mixtures whose behavior is similar to the one of organic explosives. This challenge is difficult to address, because the main feature of the reaction of nanothermites is the formation of condensed phases. According to the thermochemical data of Fischer and Grubelich, a few thermite mixtures give only gaseous species, and the unique aluminothermic composition in this regard is $\text{Al}/\text{I}_2\text{O}_5$ [1]. This shows that non metallic oxidizers could be a good alternative to metallic oxides for preparing nanothermites with high reactivity. The analysis of the results published by Prof. Zachariah's group over the past decade shows that the reactivity of nanothermite is strongly increased by replacing metallic oxides by oxygenated salts such as perchlorates and periodates [40,42,44,55,79,80]. The high pressurization rates produced by these compositions in closed vessel, suggests that they have also higher flame propagation velocities than nanothermites produced from metallic oxides.

The concept of "negative explosives" introduced by Shimizu [81] could be explored with nanopowders. For instance, the use of oxygenated salts considered as non-oxidizing at low temperatures, such as sulfates or phosphates, leads to reactive compositions when mixed with aluminum nanopowder.

The nature and the particle size of the oxidizer is not the only way to explore to develop new nanothermite compositions. The morphology of the oxidizer particles, and the way they are arranged with the aluminum nanoparticles have a significant influence on their reactive properties. Although the studies on this topic are still scarce, they show the interest of this approach. For instance, composite oxidizer particles can be used for tuning or increasing nanothermite reactivity. Prakash *et al.* have produced composite nanoparticles thanks to a spray process, with a permanganate core surrounded by a ferric oxide shell. In this research, the authors have played both on the composition and the morphology of the oxidizer [82]. This technique made possible the use of permanganate, which is an unstable compound, as oxidizer in nanothermites. Similarly, Wu *et al.* prepared particles with a perchlorate core enclosed in iron or copper oxide shell, which they subsequently mixed with aluminum nanoparticles to obtain extremely reactive nanothermites [40]. The same approach was investigated by Feng *et al.*, who coated iodine pentoxide with iron oxide [83]. More recently, Huebner *et al.* have deposited ferric ox-

ide layers of different natures on aluminum nanoparticles by a chemical process, to obtain stable core-shell nanothermites [84]. Previously, Kaplowitz *et al.* had tried to replace the alumina shell of aluminum nanoparticles by an oxidizing layer of iron oxide. This attempt had been unsuccessful, since the iron oxide shell enhanced the oxidation of aluminum core rather than inhibiting it [21]. Qin *et al.* have synthesized Al@SnO_2 and $\text{Al@Fe}_2\text{O}_3$ nanothermites by atomic layer deposition (ALD); in both cases, they observed that these core-shell materials gave more intense combustion than the homologous mixtures prepared from nanopowders [85,86]. The ALD process is of particular interest for preparing nanothermites, because it leads to an optimized contact between the aluminum nanoparticle and the deposited metallic oxide shell. Furthermore, in materials prepared by ALD, the powder keeps the high degree of porosity which is essential to obtain fast flame propagation velocities. It would be interesting to further increase the ratio oxide/aluminum, in order to see whether the oxide behaves as binder. This could be an interesting bottom-up approach for consolidating nanothermite loose powders in the form of objects. The only weak point of ALD process is its low output which is typically of one gram per day.

Despite their inorganic nature, some aluminothermic mixtures can be particularly unstable. For instance, Al-based compositions prepared from soluble peroxides (*e.g.* Na_2O_2 or K_2O_2) spontaneously ignite in contact with moisture. Aluminum also reacts exothermically with iodine. Mixtures of peroxodisulfates with aluminum give explosive reactions in contact with alkaline solutions. It can be noticed that mixtures containing chlorates are unstable in contact with concentrated acids, and those comprising permanganate can ignite in the presence of organic substances. These hazards must be always kept in mind, when preparing new nanothermite compositions.

5.2 Hybrid Compositions

Hybrid compositions are made up of a nanothermite at which an energetic gas generating agent is added. These detonating materials represent an overriding interest, not only from an academic point of view, but also on a practical standpoint for replacing primary explosives [45,87]. The nanostructured thermites and explosives (NSTEX) are prepared by dry mixing of a nanothermite with high explosives in sub-micrometer- or nanopowders (*e.g.* RDX, HMX, PETN, CL-20). Explosives can be prepared as fine powders by different techniques, but the Spray Flash-Evaporation (SFE) process developed and patented by NS3E laboratory has proven to be by far the most efficient for this purpose [88–93]. NSTEX can be considered as the missing link between pyrotechnics and explosives.

The NSTEX have unconventional properties stemming from the combination of the materials they are made of. Upon slow heating, the explosive decomposes pro-

gressively without activating the abrupt reaction of the composition. The deflagration of NSTEX can be induced by an open flame or a hot wire. Under confinement, it accelerates until reaching the detonation threshold of the explosive. The transition from deflagration to detonation always occurs in the material in loose powder state ($d < 30\%$ TMD). High porosity is necessary to ensure the fast pyrolysis of the explosive, and to limit the pressurization which slows down the deflagration of the nanothermite [94].

The nanothermite plays an essential role in the transition to detonation, by allowing it to happen in very short times and distances (5–20 mm), and with small amounts of NSTEX (< 50 mg). Once initiated, the detonation of the explosive in the NSTEX propagates at a lower velocity than the one the pure explosive would have at the same density. The heat produced by the aluminothermy reaction does not feed the detonation propagation, because it is released on a much longer time scale. On the contrary, nanothermite particles oppose resistance to the detonation propagation. A part of the energy carried by the shock wave is absorbed by the acceleration of NT particles. This effect causes a slowdown of the detonation velocity. For this reason, the detonation velocity in a NSTEX increases with the content of explosive nanopowder in the composition and, conversely, decreases with the amount of nanothermite.

The shock wave produced by the detonation of NSTEX is able to induce a shock to detonation transition in a secondary charge of PETN (Figure 4). This effect was called “pyrotechnic transduction” [45].

Hybrid compositions were also prepared by electro-spraying from an Al/CuO nanothermite and nitrocellulose,

which was used as gas generating agent and binder [95–97]. In these hybrid materials, the particles composing the nanothermite are assembled in microspheres. Wang et al. have observed that nitrocellulose favors the ignition of the composite materials and increases their reactivity when it is introduced in a small proportion (5 wt.%). [96]

Berthe *et al.* have coated propellant grains (Vectan A1) by a sulfate-based nanothermite ($\text{Al}/\text{Na}_2\text{SO}_4$). This hybrid material ignited easier and burnt much faster than the pure propellant tested in the same conditions. In addition, combustion propagation was tuned by mixing coated and uncoated propellant grains, in different ratios [98].

5.3 Understanding the Reactions

The research carried out in the field of nanothermites and hybrid compositions over the two past decades has evidenced the atypical properties of these new energetic materials and has led to the development of processes for preparing the necessary elementary bricks. One of the most prominent current issues is now to understand the underlying reaction mechanisms of these compositions, from the atom level to the scale of final charges.

Numerous challenges are addressed for understanding how really work these materials. The chemical nature of the components, their crystal properties, the surface chemistry of particles, the reaction of elementary particles, the interactions between the fuel and the oxidizer, the heat propagation inside the charge and the confinement are the major parameters that should be investigated. These reactive systems have much higher level of complexity than classical explosives. For this reason, the reaction of nanothermites and hybrid compositions is extremely hard to model. The task is made even more difficult by the lack of experimental input data and still too low computing power.

In forthcoming years, the study of mechanisms will be mainly focused on the acquisition of experimental data that will be essential for future modeling.

The first step is the morphological characterization of the nanopowders used as nanothermite components. Scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) give valuable information on the shape and the size distribution of nanoparticles, while X-ray diffraction on powders is used to determine their crystalline nature. The determination of the specific area of the components and the mixture thereof by gas adsorption (BET method) provides representative information on the interactions between the phases in the composition.

The second step is the thermogravimetric analysis (TGA) of the components. This technique is used for different purposes, such as: (i) the evaluation of the amount of adsorbed species on nanopowders; (ii) the titration of constitution water in hydrated salts or hydroxides; (iii) the determination by oxidation of the metal content in the fuel nanopowder;

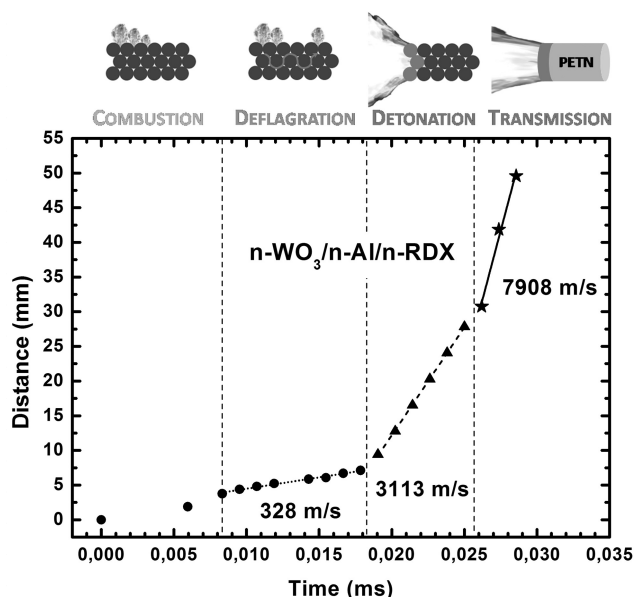


Figure 4. Experimental curve representing the pyrotechnic transduction from the NSTEX to the detonation of a PETN secondary charge.

(iv) the interaction of the fuel with atmosphere; and (v) the decomposition of the oxidizer upon gradual heating.

The third step consists to use more specific analytical techniques, for the advanced characterization of nanothermites and their derivatives. These techniques require samples from few milligrams to grams. The “T-jump” technique consists to heat quickly (10^5 to 10^6 K/s) by resistive heating a small amount of nanothermite deposited on a platinum wire. The ionized reaction products are collected and analyzed by mass spectrometry [99]. The tests in closed vessel are generally performed on samples of some tens of milligrams, which are ignited by a hot wire or a laser. A Kistler’s sensor and a photodiode operating at high frequencies are respectively used to measure the dynamic pressure and the evolution of the light intensity during the reaction. The measure of the pressurization rate permits to compare the reactivity of different nanothermites, provided to work with the same loading density. For instance, the results published by Prof. Zachariah’s group, which are performed in similar operating conditions, show that nanothermites prepared from metallic oxides are less reactive than those prepared from oxygenated salts as potassium permanganate or periodate, and that hybrid compositions prepared from nitrocellulose are more reactive than the nanothermite from which they are prepared [17]. Particular attention should be paid to the amount of sample used for performing tests in pressure bomb, because this parameter influences the combustion mode and can sometimes lead to inconsistent results. For example, a K_2SO_4/Al composition produces a much lower pressurization rate than a $K_2S_2O_8/Al$ composition (2517 times less) [100]. This probably arises from the fact that the amount of K_2SO_4/Al sample is not enough for reaching the strong reaction mode of this composition. This analysis is supported by flame propagation velocity measurements in tubes, which showed that the combustion front travels at 351 m/s and 510 m/s in Na_2SO_4/Al and $Na_2S_2O_8/Al$, respectively [43]. Tubes used for studying the flame propagation velocities in nanothermites or hybrid compositions are made of a transparent matter such as poly (methyl methacrylate) [45], polycarbonate [56,59] or glass [101]. The ideal internal channel diameter is of 3 to 5 mm, which has the triple-edge advantage to facilitate the tube loading, to reach a flame propagation velocity close its maximal value [102] and to limit the amount of composition needed. The optimized tube length is 100 to 150 mm, which allows the combustion front to attain a steady value (with loose powder) and to observe the detonation propagation in hybrid compositions. For the same reason, the loading with loose powders should be preferred to the loading with pressed powders. The propagation of flame front is recorded by high speed video operating from 20,000 to 1,000,000 fr/s, depending on the phenomena observed. The analysis of experimental films provides the distance travelled by the combustion as function of time, which permits to identify the reaction modes and the corresponding transitions, and to calculate the velocity or the ac-

celeration/deceleration of the reaction front. Sullivan *et al.* have recently proposed an “extended burn tube (EBT) test” in order to obtain quantitative information on the combustion of energetic nanocomposite materials [103]. The experimental setup consists in long tubes, with typical length of 1.8 m and inner diameters ranging from 1.56 to 4.76 mm, which are capped on their ignition end. Small amounts (25 to 250 mg) of an Al/CuO nanothermite in loose powder state are placed in the tube, of which only a small portion is filled by the reactive composition. After ignition, the flame front expands in the unfilled part of the tube, in the direction of its open end. This effect, which was called “reactive entrainment”, is attributed to the fact that the reaction time is longer than the momentum relaxation time of particles. The propagation of the luminous front occurs in two steps. At first, the luminous front travels with a steady velocity until it reaches a point called “quench distance”. The “burn time”, which is an intrinsic property of the composition, is finally calculated by dividing the quench distance by the initial velocity. The measure of the heat released by the reaction of nanothermites is carried out in calorimeter bomb on samples of typically 1 to 3 grams. The combustion of a propellant grain insures an efficient and reliable ignition of the nanothermite sample. The main difficulty relies in the cleaning of the stainless steel crucible in which the reaction takes place, owing to the formation of the solid residues splashed at molten state, which sometimes strongly adhere to the crucible walls. After a calorimetric experiment, the calorimeter bomb must be opened with particular caution, under a fume hood. These precautions are necessary to avoid inhaling toxic substances that form in the oxygen-lean atmosphere of the bomb. Hydrogen cyanide or white phosphorus can form in such conditions from compositions containing nitrogen or phosphorus compounds. The characterization of hybrid materials in a calorimeter bomb is dis-adviced by reason of the destructive effects their detonation could have on the system.

In conclusion, the characterization of nanothermites has many facets. It must always be performed considering the material as a whole, from the atom to the final object. This can be done by systematically establishing correlations between the morphology and the pyrotechnic behavior at all scales.

5.4 Sensitivity Concerns

The degradation of nanostructured aluminothermic compositions is activated at temperatures higher than 450°C , at which solid state aluminum oxidation starts. In consequence, nanothermites are relatively insensitive to heat; they react without deflagrating when they are submitted to progressive heating. This behavior is a pledge of security for hybrid compositions containing high explosives, which decompose at temperatures lower than 350°C . In other words, the decomposition by the slow heating of hybrid composi-

tions occurs by a sequential mechanism that does not involve synergistic effects between the decomposition of the explosive and the reaction of the nanothermite.

Nanothermites are usually quite insensitive to the impact of a fall-hammer. Their low sensitivity to impact comes from the inorganic nature of their components, but also from their low density at loose powder state, which cushions the impact and absorbs a part of the mechanical energy brought to the sample. The addition of different organic explosives strongly sensitizes Al-based nanothermites to impact.

Most nanothermites are very sensitive to friction. In aluminum based nanothermites, the sensitivity thresholds strongly decrease with the size of oxide particles. This sensitization is only observed when oxide nanoparticles are intimately mixed with aluminum nanopowder. The nanothermites which contain large, undissociated agglomerates of oxide nanoparticles behave as thermites prepared from micrometer-sized oxidizer. When nanothermites are mixed with explosives, the sensitivity depends on ratio nanothermite/explosive. Explosive lean mixtures are more sensitive than the nanothermite alone, while explosive rich mixtures generally have lower sensitivity, with thresholds close to the one of the pure explosive.

An extreme sensitivity to electrostatic discharge (ESD) is a distinctive feature of aluminum based nanothermites, making them hazardous to handle. One of the most sensitive nanothermite is Al/Bi₂O₃ whose sensitivity thresholds decrease strongly with the size of bismuth trioxide particles, and is below micro-joule level for sub-micrometer sized Bi₂O₃ particles [62]. The mixing of an ESD sensitive nanothermite (Al/WO₃) with a high explosive nanopowder (RDX) results in a significant increase of the threshold (desensitization) to this kind of stress [45]. A good laboratory practice is to work in a damp atmosphere, with hygrometry rate higher than 60%, to limit the hazards coming from electrostatic charges.

6 Future Challenges

Future challenges in the field of nanothermites are of theoretical and applicative natures. Past research has already reached a degree of maturity, which allows the integration of nanothermites and of their derivatives within pyrotechnic systems in a relatively short-term. However, many concepts remain to be experimentally explored and modeling of the reactions of nanothermites is still at a very early stage. Finally, a cross-cutting aspect of paramount importance will be the experimental study of toxicological aspects related to the use of nanopowders in pyrotechnic compositions.

6.1 Development of new Concepts

The research effort in the domain of nanostructured aluminothermic compositions should expand in three main directions: (i) the preparation of materials; (ii) the study of new properties and (iii) the development of characterization means.

In the forthcoming years, the preparation of new nanothermites will remain the principal challenge, which will consist in putting the bricks, which can be simple or complex, at the good place. The emphasis will be put on the use of components, *i.e.* fuels or oxidizers, which have not been yet employed in the form of nanopowders for preparing nanothermites, but the main breakthroughs will come from the structuring and the organizing of the matter. The shape of fuel and oxidizer particles has a strong influence on the reactivity of nanothermites [59]. Till now, most of nanothermites described in literature were prepared from "spherical" oxide nanoparticles. It should be interesting to test particles with a different morphology, such as fibers, tubes or flakes. The case of most complex structures should be considered: For instance, spray techniques can be used to assemble nanoparticles in hollow spheres or to prepare core-shell structures [40,82,104]. The particle recognition, which is based on electrostatic interactions, can be used for assembling fuel and oxidizer in an orderly manner [63]. At larger scale, the aim is to find processes for moving from nanothermite powders to objects that can be more easily integrated in systems. An example of this approach was given recently by Comet *et al.*, who developed a chemical process to transform an Al/WO₃ nanothermite powder into solid porous foam [31].

Up to now, the reaction of nanothermites was only studied on small samples, from a few milligrams to some grams [17]. Larger scaled experiments were not reported in literature. The reason is that nanothermites have low sensitivity thresholds, especially to friction and electrostatic discharge, which make their preparation hazardous in large amounts, such as hundreds of grams or kilograms. However, experimenting on large nanothermite charges should bring thrilling breakthroughs in this domain of research. Measuring the pressure and the temperature produced by the reaction of nanothermites and hybrid compositions, with high spatial and time resolution, is necessary for understanding the reaction mechanisms [105]. Determining the sound velocity in such compositions could give valuable information to define whether nanothermites can detonate or not, even though the analysis of existing data, which was performed by Khasainov *et al.*, has led to conclude this was not possible [23]. Recently, Gottfried *et al.* have inferred extremely high detonation velocity on hybrid nanocomposite materials Al/CuO/nitrocellulose (11.7 km/s) primed by a laser-induced air shock [106]. These experiments were performed on milligram samples; they are probably not representative of what would happen with a real charge. However, the possibility to detonate large nanothermite or hybrid com-

position charges, pressed at high TMD levels, should be studied experimentally before drawing any conclusions on the observation reported by Gottfried *et al.* One other aspect which should be interesting to investigate is the electromagnetic radiation released by the combustion of nanothermites. Indeed, Korogodov *et al.* have evidenced that the reaction of an iron-aluminum thermite mixture emits a micro-wave radiation in the range of 3.4 to 37.5 GHz [107]. According to these authors, this effect depends on the surface of reactants. In other words, it should be enhanced by using thermites prepared from nanopowders. The phenomenon observed by Korogodov *et al.* has perhaps an influence on the deflagration of thermites.

6.2 Applications and Integration in Systems

Nanothermites and hybrid compositions are new energetic materials, whose performance goes beyond the range covered by classical pyrotechnics. The outstanding versatility of these compositions arises from the chemical variety of components which can be used to prepare them.

The most important and promising application is the replacement of explosives and compositions containing toxic metallic compounds in the marketed priming systems. Numerous transition metals are of very high concern for human health. In forthcoming times, regulations will strongly limit or even prohibit the utilization of metals commonly used in pyrotechnics, such as lead or chromium. This is the reason why the development of “green” compositions has become the number one priority of pyrotechnics industry (Figure 5A). Hybrid compositions like NSTEX are amongst the most promising substances for this purpose. The technical challenge to overcome is now to stabilize the porosity of such materials, which is a critical problem needing to be solved. A first attempt consisting to prepare nanothermites as solid porous foams (Figure 5B) was recently described by Comet *et al.* [31].

Another application of nanothermites and hybrid materials is the preparation of compositions for electrical or percussion priming systems, used to ignite propulsive powders [108]. Energetic materials for primers must be sensitive to the kind of stress applied to activate these systems and release hot gases and particles.

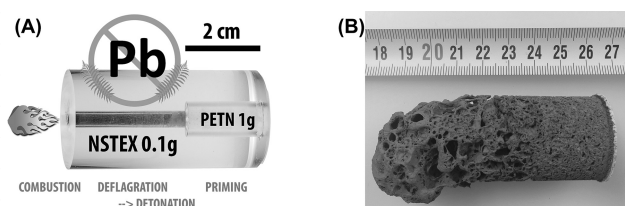


Figure 5. Experimental device used for lead-free priming of PETN (A); photograph of a nanothermite foam (B).

Nanothermites and their derivatives can be also used as fast burning compositions for short pyrotechnics delays [109], with time bases ranging from milliseconds to microseconds per centimeter. The slowest fast delay systems could be prepared from gasless nanothermites such as Al/Cr₂O₃ [110,111], Al/NiO [112], or red P/Fe₂O₃ [113]. The velocity can be adjusted by playing on the composition, the particle size of components and the density of mixtures. The absence or a limited amount of gases is necessary for having a stable deflagration. On the other hand, extremely short and precise delays could be obtained with hybrid compositions. In this case, the detonation wave travels faster than gases, which means that the latter do not influence the propagation velocity.

Aluminum nanopowder can be used in aluminothermic mixtures for propulsion applications. Risha *et al.* have observed that the combustion of aluminum/water compositions propagates with slow velocities from 1.5 to 8.6 cm/s, which increase with argon pressure in the test chamber [114]. In a more recent research, Risha *et al.* have observed that Al nanopowder slowly oxidizes in the contact of water. An apparent passivation is reached after several days; however this illustrates the metastability of such compositions. Once passivated, the mixture is cast and frozen at −35 °C to prepare an aluminum/ice (ALICE) propellant block [29]. This technique was used by Pourpoint *et al.* to propel an experimental rocket [115].

Hybrid nanothermite compositions (RDX@Cr₂O₃/nano-Al [116]) have been used by Sourgen *et al.* to shift a 40 mm projectile (m = 315 g) placed in a wind tunnel under a supersonic air flow at Mach 3. The activation of a thruster containing 0.16 g of hybrid composition, representing only 0.051 % of the projectile mass, shifted the projectile by an angle of 3° compared to its initial position [117].

In the domain of pyrotechnic security, an original concept was patented by Comet *et al.* for safe preparation of nanothermite charges used for the ignition of pyrotechnic train in warheads [118]. This process consists in mixing nanothermites components by the motion of ferromagnetic particles activated by an oscillating external magnetic field.

The pyrophoricity of non-passivated metal nanoparticles, or the one of nanothermites containing these particles, could be use for the ignition of fuel-air mixtures. In this application, the liquid used as fuel prevents the oxidation of the particle, until the liquid surrounding the particle is totally evaporated when the charge is dispersed into atmosphere. The ignition of the particle would occur at the moment when the mixing of fuel vapors with air is optimal, leading to an optimized fuel-air detonation.

Nanothermites can find numerous cutting-edge applications in the forthcoming years. Nevertheless, the regulation aspects must not impede the scientific advances in this domain, and should be well-adapted from the outset to contemporary challenges. Scientists working in the domain of energetic materials must consider regulations as a means to push forward the innovation. For instance, the REACH regu-

lation which limits the use of lead compounds has led to the development of hybrid detonating materials (NSTEX).

Finally, a broad research area in the next decade will be the toxicity assessment of the nanopowders used for preparing nanothermites and hybrid compositions. The study of the hazards related to the reaction products of these energetic materials has also a great importance. Interdisciplinary research involving close collaboration between biologists and pyrotechnicians will be necessary to achieve this end.

6.3 Toxicological Aspects

The use of nanomaterials in energetic compositions raises toxicological questions [119]. The main problem is the exposure of workers or end-users, to free nanoparticles which enter in the composition of these materials or which are released by their reaction. In nature, the living world is structured at nanoscale; nano-machineries are always part of larger, more complex systems, and are never observed as free objects. Free nanoparticles are barely found in the environment; they mainly come from natural (lightening, volcanoes) or anthropogenic combustions. Fine particles in suspension in atmosphere induce the condensation of water vapor, leading to rain, that would not exist otherwise. The precipitations decrease the concentration of fine particle in the atmosphere. In other words, fine particles are not only natural, but have also a vital role in sustaining life on the Earth.

The risk attached to the “artificial” use of nanoparticles is correlated to their nature and their concentration level. Two cases are to be considered: (i) particles which are soluble in body fluids, and (ii) the others. In the domain of energetic materials, the first type of particles corresponds to molecular explosives and soluble salts; the second type is represented by metals, metalloids, ceramics, and polymer particles. Soluble species can be metabolized by chemical processes in the human body, while the others tend to accumulate in cells, causing long term harmful effects such as inflammation, necrosis or apoptosis, which leads to generalized health problems.

Nanoparticles which pass through cell membrane are put in lysosomes which are the waste bins of cells. Depending on their chemical nature, nanoparticles are either dissolved by the internal acidity of lysosome or stockpiled in it. Metal nanoparticles are oxidized in ions which are released in the internal liquid of the cell [120], *i.e.* the cytosol, causing cellular dysfunction. Stable nanoparticles gradually clutter lysosomes making them unable to treat cellular wastes. In vitro tests show that cellular metabolism is affected by aluminum or oxide nanoparticles [17]. However, the influence of nanoparticles on complex beings cannot be extrapolated from experiments on individual cells. The hazard begins with the exposure to nanopowders. Nanoparticles can enter the body by three doors: (i) the skin, (ii) the oral

route and (iii) the respiratory tracts. These ways of entry are protected by different biological systems that limit the amount of nanomaterials likely to reach cells. Nanoparticles cannot cross epidermis, except in case of damaged skin or at the place of hair follicles. Oral route is not a common contamination route, except in case of intentional ingestion. Finally, breathing is the most dangerous way of exposure to nanoparticles. The finest particles are not trapped by the respiratory system, and can reach pulmonary alveoli. From a practical standpoint, great care must be taken in laboratories, to avoid the aerosolizing of nanoparticles and to limit their concentration in inhaled air. The use of a safety weighing cabinet is advised for handling the components of energetic nanomaterials. The sample recovery and the operations needed for loading experimental systems should be performed in the confined space of a glove box. It should be noted that the reaction of an organic nanostructured explosive releases the same products than those produced by a conventional, micrometer-sized charge of this explosive. The deflagration of nanothermites is more problematic, as it gives fumes composed of fine inorganic particles, which are often not soluble. Experimenting on the combustion of nanothermites require efficient air extraction, and appropriate protection of workers.

From the point of view of manufacturing processes, the nanopowders must be prepared and handled as far as possible in closed systems. A major challenge will be also to assemble nano-bricks in objects with larger dimensions. At the present time, the science of energetic materials is just beginning to have the nanoparticles which are the building blocks necessary to develop future pyrotechnic and explosive systems. However, one notice a growing interest in the integration of these fine particles within materials such as microspheres [121] or foams [31], in order to have no free nanoparticles.

According to the precautionary principle, a given material is always considered as more hazardous in nanoparticulate state than in a micrometer-sized form. For this reason, the research in the domain of nanothermites or hybrid compositions must move towards the choice of nano-sized components made of innocuous materials from a toxicological point of view, when it is possible.

7 Conclusions

Nanothermites mark a significant new beginning in pyrotechnics science, which was stagnating for several decades. In this domain, much remain to be discovered, the challenge being to size effects for precise needs and applications.

In the classical meaning, nanothermites are mixtures of fine powders of aluminum and metallic oxides. This narrow definition can be extended to any combustible mixtures in which a metal or a metalloid fuel is oxidized by an oxygen donor, which is often a metal-based compound. The nano-

particles of several elements can be used as fuel for nanothermites, but aluminum nanopowder is by far the most employed. This comes from the outstanding properties of this material, in terms of stability, reactivity and availability. In turn, the problem of safe handling raises the question of toxicological hazards of aluminum nanopowder.

Up to now, most of processes used to prepare nanothermites lead to random mixes. In forthcoming times, a major research effort will be necessary to order nanoparticles with different shapes and sizes in compositions. This should be performed without adding any substances altering pyrotechnic properties such as graphene oxide [63] or DNA [122], and without decreasing the porosity. One other important challenge is the stabilization of nanothermites in state of monolithic porous objects likely to be integrated in pyrotechnic systems.

Many nano-sized aluminothermic compositions were studied worldwide in the recent years. The use of aluminum nanopowder as fuel increases the reactivity of aluminothermic mixes, *i.e.* mixtures considered as not reactive can become so, and moderately reactive compositions can react violently. Several families of oxygenated or fluorinated oxidizers should still be assessed as nano-sized components of aluminothermic compositions. Another way to improve the reactivity of nanothermites is to combine them with explosive nanopowders, to form hybrid compositions (NSTEX). These detonating substances are promising for the replacement of primary explosives containing heavy metals, such as lead, cobalt or nickel.

The understanding of reaction mechanisms of nanothermites and hybrid compositions has become essential for future advances in this domain. For this purpose, intensive research should be still performed, in order to obtain the experimental substrate that will be necessary to modeling.

The problem of sensitivity is not a thrilling scientific challenge; it should be rather considered as an intermediate step between the research laboratory and the production facility.

The future advances will arise from basic and integrative research. The “academic” challenges will be related to the bottom-up building of nanothermites and their derivatives, from the scale of particles to the one of the final object. They will also consist to identify new effects, particularly in the fields of ignition and combustion propagation. The engineering challenges will focus on the integration of existing nanothermites and hybrid compositions in functional pyrotechnic systems, in order to produce them at an industrial scale.

Finally, one of the most prominent challenges for the next decade will be to assess the toxicity of nanothermite components and of their reaction products. The research necessary for this purpose will require both *in-vitro* and *in-vivo* tests and will be done in close cooperation between biologists and pyrotechnicians. This is a nice illustration of the fact that progresses in contemporary science will be

achieved by crossing the borders between scientific domains.

Author contributions

The manuscript was written through contributions of all authors. All authors contributed equally and have given approval to the final version of the manuscript.

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