

Video Article

Nanothermite with Meringue-like Morphology: From Loose Powder to Ultra-porous Objects

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Abstract

The goal of the protocol described in this article is to prepare aluminothermic compositions (nanothermites) in the form of porous, monolithic objects. Nanothermites are combustible materials made up of inorganic fuel and an oxidizer. In nanothermite foams, aluminum is the fuel and aluminum phosphate and tungsten trioxide are the oxidizing moieties. The highest flame propagation velocities (FPVs) in nanothermites are observed in loose powders and FPVs are strongly decreased by pelletizing nanothermite powders. From a physical standpoint, nanothermite loose powders are metastable systems. Their properties can be altered by unintentional compaction induced by shocks or vibrations or by the segregation of particles over time by settling phenomena, which originates from the density differences of their components. Moving from a powder to an object is the challenge that must be overcome to integrate nanothermites in pyrotechnic systems. Nanothermite objects must have both a high open porosity and good mechanical strength. Nanothermite foams meet both of these criteria, and they are prepared by dispersing a nano-sized aluminothermic mixture (Al/WO₃) in orthophosphoric acid. The reaction of aluminum with the acid solution gives the AlPO₄ "cement" in which Al and WO₃ nanoparticles are embedded. In nanothermite foams, aluminum phosphate plays the dual role of binder and oxidizer. This method can be used with tungsten trioxide, which is not altered by the preparation process. It could probably be extended to some oxides, which are commonly used for the preparation of high performance nanothermites. The WO₃-based nanothermite foams described in this article are particularly insensitive to impact and friction, which makes them far safer to handle than loose Al/WO₃ powder. The fast combustion of these materials has interesting applications in pyrotechnic igniters. Their use in detonators as primers would require the incorporation of a secondary explosive in their composition.

Video Link

The video component of this article can be found at <https://www.jove.com/video/56479/>

Introduction

This article reports on a method for transforming nano-sized aluminothermic mixtures (Al/WO₃) from a loose powder state to foams¹. Nanothermites are fast burning energetic compositions, which are most frequently prepared by the physical mixing of a metallic oxide/salt with a reducing metal, in the form of nanopowders². The most representative oxides used to prepare nanothermites are Cr₂O₃^{3,4}, Fe₂O₃⁵, MnO₂⁶, WO₃⁷, MoO₃⁸, CuO⁹ and Bi₂O₃^{10,11}, while the metallic salts used are perchlorates^{12,13}, iodates^{14,15}, periodates¹⁶, sulfates¹⁷ or persulfates¹⁸. Aluminum nanopowder is the best choice as fuel for nanothermites owing to their numerous desirable properties, such as a high oxidation heat (10 - 25 kJ/g)¹⁹, fast reaction kinetics²⁰, low toxicity²¹, and a fair degree of stability once it has been accurately passivated²².

In Al-based nanothermites, the flame front propagates at high velocities (0.1 - 2.5 km/s), but this cannot, however, be considered as detonation²³. The reaction mechanism is actually driven by the convection of hot gases in the porosity of unreacted material. In other words, the porosity is essential to the fast burning of nanothermites. However, loose nanothermite powder is not stable from a physical standpoint. They are compacted by shocks or vibrations, and their densest component (generally the oxide) progressively separates from the composition by the effect of gravity. The stabilization of nanothermite porosity is a crucial challenge for their integration in future pyrotechnic systems.

The main advantage of the preparation process described herein is to give highly porous, solid, nanothermite monoliths, which can be shaped by molding the paste from which they form. Additionally, nanothermite foams are quite insensitive to shock, friction and electrostatic discharge compared to nanothermite loose powders. This insensitivity makes them particularly safe to handle and machine, for instance by sawing or drilling.

When loose nanothermite powders are pressed or pelletized, their porosity decreases and objects are formed. The cohesion of such materials originates from the surface forces, which are responsible for the aggregation of nanoparticles. The mechanical strength of nanothermite pellets can be improved in the presence of carbon nano-fibers, which act as a framework to reinforce these objects²⁴. Unfortunately, pressing strongly decreases the reactivity of nanothermites. According to Prentice *et al.*, the pressing of nano-Al/nano-WO₃ compositions induces a collapse of their reaction velocity by two orders of magnitude⁷. In conclusion, contrary to most explosives, nanothermites cannot be shaped by pressing.

To date, very few methods for structuring nanothermites have been reported in scientific literature dealing with nanothermites. Nanothermites can be deposited on substrates, either from the powders of their components dispersed into a liquid medium by electrophoresis²⁵, or by the sputtering of their components in successive layers²⁶. Both approaches lead to dense deposits, which are less reactive than loose powders and tend to delaminate from the substrate on which they are prepared.

The preparation of "three-dimensional" objects composed of nanothermite was proposed by Tillotson *et al.*⁵, who used the sol-gel synthesis developed by Gash *et al.* that consists of gelling solutions of metallic salts by epoxides²⁷. Nanothermite monoliths are prepared by dispersing Al nanopowder in the sol, before gelling. The gels are subsequently dried either in a heat chamber to produce xerogels or by a complex process involving the use of supercritical CO₂ to obtain aerogels. Nanothermite aerogels not only have strong reactivity but can also be machined owing to their excellent mechanical properties. In addition, the sol-gel process allows one to synthesize micro- and mesoporous materials with an unrivalled degree of homogeneity between the fuel (Al) and the oxide in the mix. Despite these interesting features, the use of the sol-gel process is limited by: (i) the complexity of the batch synthesis, which depends on numerous parameters; (ii) the unavoidable presence of synthesis byproducts (impurities) in the final material, and (iii) the very long time needed by the different steps of the process.

Combustible mats of nanothermite were prepared by the electrospinning of nitrocellulose (binder) from solutions charged with Al and CuO nanoparticles²⁸. These nanothermite felts are composed of fibers with sub-micrometer scale diameters, which are *a priori* non-porous. In these materials, the porosity is defined by the entanglement of fibers. The samples of nanothermite mats burn slowly (0.06 - 1.06 m/s) compared to pure nano-sized Al/CuO mixtures in a loose powder state, in which the flame front propagates at a velocity of several hundred m/s²⁹. Finally, the use of nitrocellulose as a binder for nanothermites is not ideal, because it considerably increases their thermal sensitivity and alters their long-term chemical stability.

Membranes of nanothermites were prepared by Yang *et al.* from complex hierarchical MnO₂/SnO₂ heterostructures mixed with Al nanoparticles⁶. In these materials, the oxide phase has a very specific morphology, in which MnO₂ nano-wires are covered by SnO₂ branches. Because of its very particular structure, the oxide not only traps Al nanoparticles, but also ensures the mechanical resistance of the membrane. The preparation process of MnO₂/SnO₂/Al membranes is very simple; it consists of filtering the nanothermite contained in the liquid in which it has been prepared, using the filtration cake as a membrane.

To summarize, the only nanothermite objects mentioned in the scientific literature are deposits on substrates, aerogels, or mats. The idea of preparing nanothermites in the form of solid foams opens new horizons for the integration of these energetic materials into functional pyrotechnics systems. The foaming process reported in this article is simple to perform and can be virtually applied to any nanothermite prepared from aluminum nanopowder. The foaming agent is orthophosphoric acid (H₃PO₄), a common, inexpensive and non-toxic chemical, which reacts with nano-Al to give the cement (AlPO₄) and the gases (H₂, H₂O vapor) that create the porosity of the material¹. Aluminum phosphate is particularly stable at high temperatures, contrary to organic binders such as energetic polymers (nitrocellulose). However, AlPO₄ behaves as an oxidizer towards nano-Al at high temperature, according to the concept of "negative explosives" proposed by Shimizu³⁰.

Protocol

CAUTION: Perform all reactions described in this article in an explosion-proven chamber with an armored window that allows both visual inspection and observation of the foaming/combustion processes by high speed video. Take care regarding the experimental risk arising from the potential ignition of aluminothermic compositions and the hydrogen explosion in the air. For this reason, always work in an explosion-proven chamber equipped with appropriate exhaust ventilation. Remember that experiments on energetic materials must be carried out by experienced scientists, who are fully aware of pyrotechnic hazards, and that all tests must be performed in accordance with local laws and safety regulations. Note that authors decline any responsibility for inappropriate use of these results.

1. Preparation of an Aluminophosphate Matrix

NOTE: Experiments are performed at room temperature (15 - 25 °C).

1. Weigh 3.00 g of aluminum nanopowder.
2. **Weigh 4.00 g of a commercial solution (85%) of orthophosphoric acid (H₃PO₄) in a 150 mL beaker; add the acid dropwise with a 3 mL polyethylene Pasteur pipette.**
 1. Optionally, a volume from 0 - 2 mL of deionized water can be added to the orthophosphoric acid.
 2. Homogenize the solution by slowly rotating the beaker by hand at approximately 100 rpm.
3. Place the beaker containing the acid in the explosion chamber.
4. Pour the aluminum nanopowder weighed in step 1.1 into the beaker containing the H₃PO₄ solution.
5. Mix quickly with a stainless steel spatula; perform this step in less than one minute.
6. Close the explosion chamber immediately.
7. Wait until the foaming reaction occurs.
8. Afterwards, wait an additional 10 min for the aluminophosphate matrix to cool.
9. Remove the beaker from the explosion chamber using a laboratory bow tong.
10. Recover the sample, which adheres to the beaker wall, by carefully breaking it. Beware of the presence of acidic residues and do not handle the materials without gloves.

2. Synthesis of Nanothermite Foams

NOTE: Experiments are performed at room temperature (15 - 25°C).

1. **Preparation of the nanothermite mixture**

1. In a 100 mL round-bottom flask, weigh 3.00 g and 3.45 g of Al and WO_3 nanopowders, respectively.
2. Mix the nanopowders with a vortex mixer operating at 2,500 rpm.
3. Gently stir the mixture with a stainless-steel spatula to homogenize it. Avoid any friction between the glass wall of the round-bottom flask and the spatula during this operation.
NOTE: In this step, the experimenter must be grounded in order to avoid any electrostatic discharge, which could cause the ignition of the mixture.
4. Repeat the operation 2.1.2.

2. Preparation of H_3PO_4 solutions

1. Weigh 4.00 g of a commercial solution (85%) of orthophosphoric acid (H_3PO_4) in a 150 mL beaker; add the acid dropwise with a 3 mL polyethylene Pasteur pipette.
2. Preparation of diluted H_3PO_4 solutions:
 1. Take the sample prepared in step 2.2.1 and add 0 to 2 mL deionised water with a 1-mL polyethylene Pasteur pipette.
 2. Homogenize the solution by the slow rotation movement of the beaker applied by hand at a speed of about 100 rpm.

3. Preparation of nanothermite foams

1. Place the beaker containing the acid prepared in step 2.2 in the explosion chamber.
2. Pour the nanothermite prepared in step 2.1 in the beaker containing the H_3PO_4 solution.
3. Mix quickly with a stainless-steel spatula; perform this step in less than one minute.
4. Close the explosion chamber immediately.
5. Wait until the foaming reaction occurs.
6. Afterwards, wait an additional 10 min for the cooling down of the nanothermite foam.
7. Remove the beaker from the explosion chamber with a laboratory bow tong.
8. Recover the sample, which adheres to the beaker wall, by carefully breaking it. Beware of the presence of acidic residues and avoid handling the materials without gloves.

3. Combustion of Nanothermite Foams

1. Place the aluminophosphate matrix prepared in step 1.10 or the nanothermite foam prepared in step 2.3.8 in the explosion chamber.
2. Place a pyrotechnic igniter close to the sample from step 3.1.
3. Close the explosion chamber.
4. Connect the igniter to a secure electronic device.
5. Fire the pyrotechnic chain.
6. Observe the combustion through the armored window with an ultrafast camera operating at 10,000 to 30,000 frames/s.

Representative Results

The aluminophosphate matrix contains crystallized aluminum (Al) and aluminum phosphate (AlPO_4). The presence of these phases was confirmed by X-ray diffraction (**Figure 1**). Additionally, gravimetric experiments have shown that this material also contains a non-crystalline part, which is amorphous alumina. In these materials, aluminum phosphate behaves both as binder and oxidizer. The oxidizing properties of AlPO_4 were evidenced by measuring the explosion heat (3,340 J/g) of a 50/50 wt./wt.% nano-Al/ AlPO_4 mixture in a bomb calorimeter¹.

The water, which is added to dilute the H_3PO_4 solutions, decelerates the rise in temperature of the reaction medium (**Figure 2**). The drying of H_3PO_4 by phosphorus anhydride (P_4O_{10}), or by any strong desiccant, is not advised (**Figure 2**, leftmost curve). In the absence of water, the paste undergoes very rapid heating, which provokes the ignition of the energetic foam and a hydrogen explosion in air. Please note that the mass of hydrogen released by the preparation of a nanothermite foam sample of 10 g is approximately 0.5 g and that the combustion of such an amount of this gas in air gives an energy of about 60 kJ. The flammability limits of hydrogen range from 4 to 75 vol.% in air and its ignition temperature is between 500 and 580 °C³¹.

The systems prepared with water are easier to mix, owing to a more favorable liquid/powder ratio. Water delays the foaming reaction and makes it more progressive and safer. Nanothermite foams produced from diluted solutions have better mechanical strength but expand less. The analysis by X-ray diffraction of nanothermite foams reveals that they contain crystallized aluminum, aluminum phosphate, and tungsten trioxide (**Figure 3**). The latter does not chemically interact with the foaming reaction.

The composition of the aluminophosphate matrix (nano-Al/ AlPO_4) and the nanothermite foam (nano-Al/ AlPO_4 /nano- WO_3) prepared according to the protocol are given in **Table 1**. The density of the foams depends on the experimental conditions in which they have been synthesized, in particular of the concentration of the H_3PO_4 solution. It typically ranges from 5 to 20% of their theoretical density, corresponding to a high porosity (80 - 95%).

The heat released by the combustion of the aluminophosphate matrix and the nanothermite foam, which were prepared according to the experimental protocol are equal to 3.4 kJ/g and 2.5 kJ/g, respectively. The combustion of foams in the calorimetric bomb produces residues containing phosphorus, whose presence is characterized by the continuous emission of white fumes in contact with atmospheric oxygen. Phosphorus is produced by the reduction of AlPO_4 inside the closed chamber, in the absence of air.

Aluminophosphate matrices and nanothermite foams are not particularly sensitive to friction and shock stresses. However, they must be handled with care owing to their moderate sensitivity to electrostatic discharge and heating sources, such as an open flame. Their combustion produces large fireballs with flying sparks made of molten particles. The impact of these incandescent phases alters the surface of the armored window of the explosion chamber.

The combustion experiment described in the experimental protocol qualitatively illustrates the fast combustion of aluminophosphate (or nanothermite) foams. It cannot be used to measure the flame propagation velocity in nanothermite monoliths because the abundant fumes released by the reaction hide the flame front. Moreover, the combustion follows several paths inside the material porosity, which makes it difficult to know where the combustion front is at a given time and, consequently, to measure a propagation velocity.

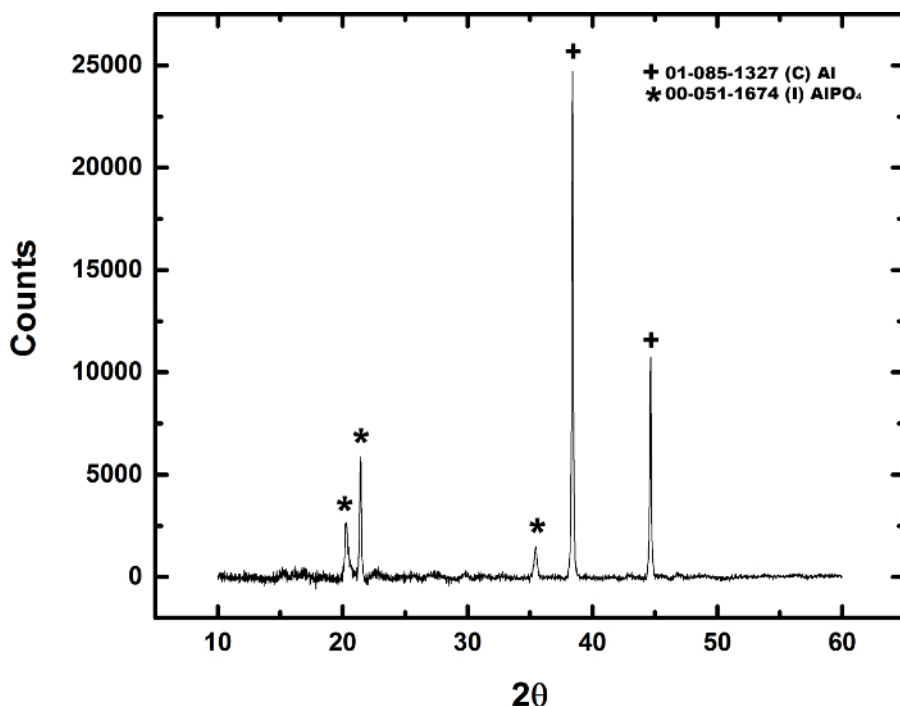


Figure 1: X-ray diffraction pattern of an aluminophosphate matrix. X-ray diffraction pattern of an aluminophosphate matrix, showing the presence of crystallized Al and AlPO₄. This figure has been modified from Comet *et al.*¹ The diffractogram was performed on a foam, which had been previously crushed into fine powder with a particle size distribution below 200 μm. [Please click here to view a larger version of this figure.](#)

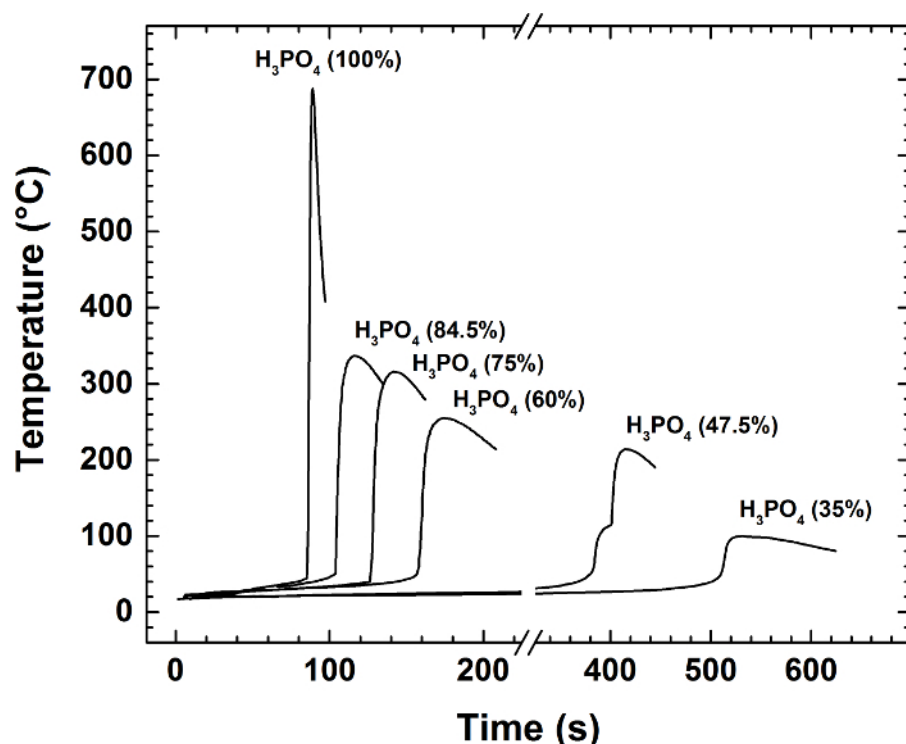


Figure 2: Evolution of temperature for nanothermite pastes during their foaming reaction. Evolution of the temperature for nanothermite pastes during their foaming reaction, depending on the H_3PO_4 concentration. This figure has been modified from Comet *et al.*¹ The temperature was measured with a type K thermocouple placed in the paste and connected to a proportional-integral-derivative (PID) controller. The runaway of the foaming reaction is observed when temperature is higher than 40 °C. [Please click here to view a larger version of this figure.](#)

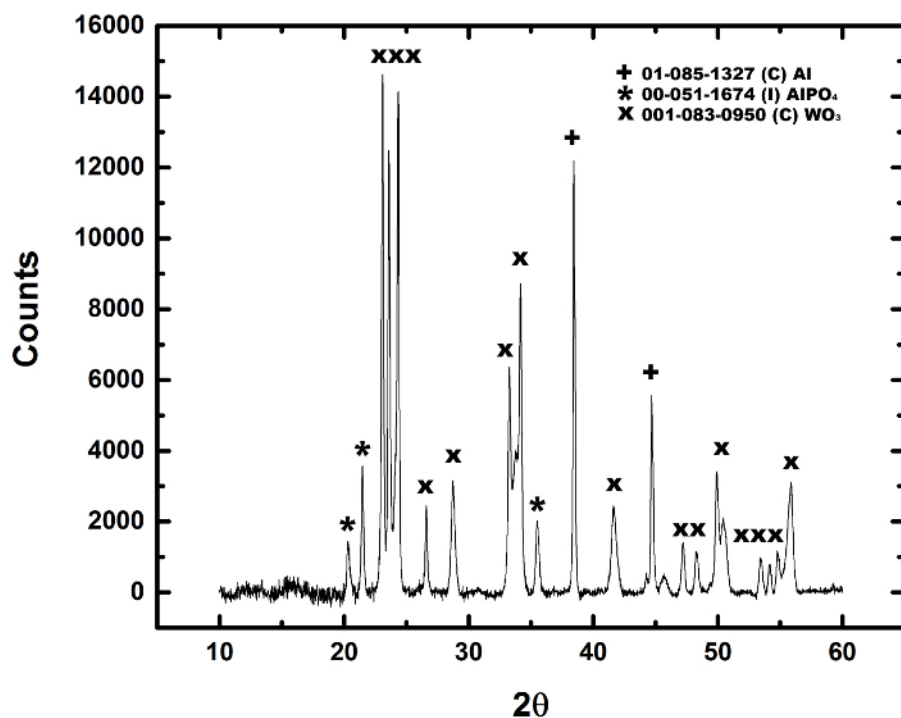


Figure 3: X-ray diffraction pattern of a nanothermite foam. X-ray diffraction pattern of a nanothermite foam, showing the presence of crystallized Al, AlPO_4 and WO_3 . This figure has been modified from Comet *et al.*¹ As for aluminophosphate foams, the diffractogram was performed on a sample, which has been previously crushed into fine powder with a particle size distribution below 200 μm . Note that tungsten trioxide does not react with orthophosphoric acid in the experimental conditions used. [Please click here to view a larger version of this figure.](#)

Sample	Al (wt.%)	Al ₂ O ₃ (wt.%)	AlPO ₄ (wt.%)	WO ₃ (wt.%)	H ₂ O (wt.%)
Al/H ₃ PO ₄ ·H ₂ O	21.8	9.4	68.8	0.0	0.0
Al/WO ₃ /H ₃ PO ₄ ·H ₂ O	14.6	5.0	44.2	36.2	0.0

Table 1: Chemical composition of the aluminophosphate (nano-Al/AlPO₄) and nanothermite (nano-Al/nano-WO₃/AlPO₄) foams prepared according to the protocol. These values were calculated from thermogravimetric data.

Discussion

The mixing process of nanopowders with acid and the closing of the explosion chamber must be performed quickly, for safety reasons. The reaction delay may vary to some extent (1 - 10 min), depending on experimental conditions. It is shortened when room temperature is too high or in the presence of external heating sources like a spotlight, which can cause early activation of the foaming reaction. Conversely, it is increased when room temperature is low. In the case of too much foaming delay (> 15 min), the reaction can be stopped by quickly pouring a large amount of water in the beaker (100 mL). The preparation of the aluminophosphate matrix or nanothermite foam must be performed at room temperature (15 - 25 °C), knowing that the foaming reaction is activated when the temperature of the paste is between 40 to 45 °C (**Figure 2**). The foaming reaction is preceded by a warning sign, which is a slight expansion of the paste with bubbles of gas breaking its surface. The reaction runaway is characterized by a fast and strong expansion of the paste, accompanied by important gaseous release (H₂ and H₂O vapor).

The quantity of nanopowder mixed with the H₃PO₄ solution defines the consistency of the paste. Low ratios of powder/acid give liquid pastes, whereas low ratios of acid/powder make mixing difficult. The oxide used for nanothermite preparation must be compatible with orthophosphoric acid. The aluminophosphate or nanothermite foams must always be prepared in small amounts (typically 10 g), to minimize the explosion hazard arising from the hydrogen released into the air during the process.

The first critical step is the weighing of nanopowders, which must be carried out by an operator wearing appropriate individual protective equipment (FFP3 filter cartridge mask) under a fume hood. The mixing of nanopowder(s) with orthophosphoric acid must be done quickly to have time to close the explosion-proven chamber, which is more difficult when the paste is thick, for instance with a high powder/acid ratio. The foams must be synthesized away from heat sources, due to the formation of hydrogen by the reaction. All energetic samples must be handled with care; nano-Al/nano-WO₃ loose powder has a particularly low sensitivity threshold to electrostatic discharge (0.14 mJ). Finally, the burning test of foams must be performed in a combustion chamber that is equipped with an appropriate air exhaust.

The preparation of nanothermite objects by this process is unique. The only other method for preparing large nanothermite monoliths is sol-gel methodology. This technique requires specific precursors and very long synthesis/drying steps, which makes it very expensive. In addition, materials produced by the sol-gel technique always contain impurities coming from the process. Finally, sol-gel product porosity is extremely small compared to nanothermite foams, which limits the propagation by convection mechanisms (pressure losses) and may alter its reactivity.

The future integration of nanothermite foams in pyrotechnic systems will require the use of other oxides (e.g. CuO and Bi₂O₃) in order to enhance their reactive properties. Furthermore, the addition of secondary explosives in nanothermite foams, either in the composition process or by subsequent infiltration (from a solution) of a pre-existing foam, could be used to synthesize detonating energetic nanocomposites³². Such materials could find interesting applications in lead-free primers. The molding of nanothermite foam into objects with well-defined shapes will be the next challenge to overcome.

Disclosures

We have nothing to disclose.

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