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A Review of Nano-Structured Thermites and Explosives: Synthesis and Emerging Applications

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Abstract

Lead-based primary explosives are highly common in the military, mining and pyrotechnics. However, lead is non-biodegradable and poses a serious threat to the environment and living beings. Lead is a potent neurotoxin that causes organ damage and affects cognitive development in humans. It contaminates the air, water and soil, thereby affecting the flora and fauna through bioaccumulation and food chain contamination. It is also notorious for degrading soil fertility and biodiversity. The search for a greener alternative landed on nanostructured materials, fuelling considerable research in this domain. Although their large-scale manufacturing is challenging, these materials promise enhanced performance, safety and reliability over existing systems. The SFE method has been identified as a major breakthrough in facilitating mass-scale manufacturing of such explosive nanoparticles with decent productivity. Coating these nanoparticles with nanothermites resulted in a benign alternative with improved performance over traditional lead-based explosives, called NSTEX. This eliminates the risk of lead contamination while also improving the explosive performance. Despite the success of this system, stabilising these mixtures into operational systems has remained a challenge, hindering its application. A breakthrough in this aspect could be a significant step forward in greener and safer pyrotechnics for the future.

Keywords: Nanoparticles, Nanothermites, Pyrotechnics, Green Synthesis.

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1. Introduction

The detonation parameters of lead salts have seen it become the most common primary explosive in military and pyrotechnic applications. However, lead is a heavy metal that adversely affects living beings and the environment [1]. With the growing need for "smart materials" with better performance, safety and reliability while also being environmentally friendly and sustainable, nanomaterials have come to the fore in science and technology. The exploration of nano and submicron particles has proven fruitful in this aspect on account of their enhanced performance while being less sensitive to external stimuli [2]. Nanomaterials have proven to be highly energy-dense and efficient, while also being considerably safe, which has led to them being a major focus of energy studies in recent years [3].

Nanothermites, also known as superthermites or Metastable Interstitial Composites (MICs), are highly reactive solid-phase energetic materials composed of nanometric metallic fuels and oxidising agents. These have high energy density, surface-area to volume ratios, energy release rates and sensitivity to stimuli in comparison to micrometric thermites [4]. However, nanothermites often undergo agglomeration before ignition, have long ignition delays and incomplete combustion [5]. However, these challenges could be overcome by mixing explosive nanopowders with nanothermites to produce a composite called NanoStructured Thermites and Explosives (NSTEX) [6].

Despite the vast improvements offered by this composition, the preparation and crystallisation of such particles have been a constant challenge. Multiple routes of preparation were found to be either too expensive or too controlled to be carried out on a large-scale manufacturing. A major milestone in this aspect was achieved at the NS3E laboratory in the form of the development of the Spray Flash Evaporation method. This method has been found to produce different types and morphologies of nanomaterials, and consistent efforts are still being made to understand the mechanism of this method and to better tune the product composition and morphology with this method [7].

Although major steps have been taken in this field, the industrial application has not been explored much, mainly due to the lack of clarity in the studies and due to the lack of a comprehensive overview of the advancements made thus far. These mixtures are an inevitable part of future defence and warfare and serve to be explored more for unlocking their maximum potential in shaping the future of energetic materials and explosives.

2. Synthesis of NSTEX

2.1. Preparation of Fine Explosive Powders

Despite the preparation of multiple top-down and bottom-up methods for the synthesis of nanoparticles, they proved to be highly ineffective in an industrial setting due to a variety of factors, including high impurity levels, safety concerns and contamination, among many others. Many spray techniques could overcome these challenges, but were highly reliant on specific solvents and supercritical fluids such as Carbon dioxide (CO_2), while their yield was also limited. This was a major setback in the advancement of NSTEX until the discovery of the Spray Flash Evaporation method[8].

The SFE method facilitated the preparation of fine and pure explosive powders at a considerable rate of formation, which was around 0.1Kg per hour [3]. This method could create a variety of products ranging from entirely crystalline products to semi-crystalline and even co-crystalline products. This depended upon the physical and chemical properties of the nanoparticles prepared in the process and their intermolecular interactions. Pure crystalline products may be prepared by employing single molecules that are not subject to these molecular interactions[9]. The basic principle of this method is the rapid evaporation of an aerosol mixture of a pre-heated solvent in which the explosives are dissolved. The solvent, while being suitable to dissolve the explosive materials, also has to be highly volatile at the temperature and pressure conditions created inside the chamber. This rapid evaporation of the solvent induces the rapid crystallisation of the explosive material. This rapid rate of crystallisation ensures that the particles have little to no time to grow, thereby ensuring that the particle size of the prepared explosives stays around 50 nm to 1 µm. Due to its suitable physicochemical properties, acetone is the most commonly used solvent for SFE to prepare explosive nanopowders. Particles prepared by this method include Trinitrotoluene (TNT), Hexogen (RDX), Octogen (HMX), Pentaerythritol tetranitrate (PETN), Ammonium dinitramide (ADN), Hexanitrohexaazaisowurtzitane (CL-20), etc. [2, 10-12].

The primary advantage of SFE is the single-step formation of fine, homogenous propulsive powders with different particle morphology. This versatility is combined with almost immediate molecular recognition times, which makes this method highly suitable for producing pure nanoparticles as well as co-crystals with well-defined morphology and composition. This could be seen in the co-crystallisation of HMX and CL-20 at 1:2 mol/mol and in the single-step formation of a core-shell particle of hexolite with an RDX core and TNT shell [13,14].

2.2. Preparation of Nanothermites

Thermites are highly energetic metal or metal-based oxide particles. In the nano size, these possess extremely high energy densities and are fine combustible powders which contain a significant amount of metallic species and may be used as fuels or oxidisers owing to these favourable properties. It is also notable that these have variable burning rates which may be tuned accordingly by calibrating the fuel and oxidiser particle size, composition and packing density[15]. While Aluminium remains the most used metal, oxidisers such as CuO, Fe_2O_3, MoO_3, Bi_2O_3, and WO_3 have also been used[16].

Nanothermites may be prepared by the physical mixing method, which involves dissolving these powders in an inert volatile liquid. This mixture is then sonicated to ensure uniformity and small size. The liquid is then evaporated swiftly to promote the formation of nanothermites. However, this method may lead to particle aggregation and may require nanoscale powders to begin with[15]. Another suitable method is called arrested reactive milling, which helps produce fully dense materials with low oxide content. In this reaction, the metal and oxide are milled in a shaker mill along with a lubricating and cooling agent such as hexane. However, care must be taken to ensure that milling is stopped before ignition to avoid accidental explosions[17].

2.3. Formulation of NSTEX

Nano-structured thermites and Explosives (NSTEX) are prepared by mixing fine explosive powders prepared by the SFE method with nanothermites. These hybrid energetic nanocomposite materials are formulated by a method known as dry mixing. Liquids are kept away during this process to avoid the growth of the explosive particle upon dissolution. The components are mixed in a vortex and manually crushed with a spatula until a homogenous mixture is created.

Loosely pressed NSTEX powders exhibit the ability to detonate by means of a transition from deflagration to detonation. The nanothermite initially undergoes deflagration and produces energy sufficient to lead to detonation of the fine explosive powder. Upon initiation, the nanothermite coating gets ignited. This fast combustion or deflagration gains enough energy to activate the detonation of the fine explosive powder. This detonation wave propagates rapidly through the NSTEX charge and may be used as a primary explosive to ignite a less sensitive secondary charge such as PETN. The propagation velocity of the NSTEX charge depends on the nanothermite to explosive ratio and also on the density of the explosive charge. Hence, the propagation velocity is a variable measure that can be adjusted accordingly by varying these factors to suit the needs of the system [3].

NSTEX is a greener and more efficient primary explosive in comparison with the heavy metal salts, such as Lead and Cobalt compounds, which are currently used for the purpose. However, these have been found to be extremely harmful to the environment, and the development of green solutions to this has been a concern in recent years. NSTEX offers a great fit in this regard as it can be produced from benignant compounds such as Calcium and Potassium sulfates, PETN, and aluminium [18].

Table 1 represents an experimental detonating device kept inside a transparent tube and observed using a high-speed camera. The system contained 4 layers – the first being completely made up of ignition nanothermite, the second being a loose NSTEX mixture, the third being a compact mixture of the same, and the fourth being a PETN secondary charge. The nanothermite employed in the study was nano-Al/nano-CuO, and the experimental device was 50mm long, with the first and third layers being 5mm long each, while the second and fourth layers were 20mm long each.

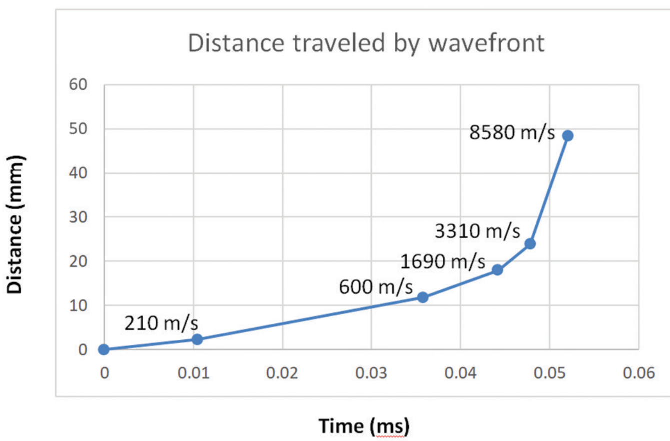

Table 1. 1) Burning of the ignition nanothermite 2) Defagration of the NSTEX mixture 3) Detonation of NSTEX 4) Accelerated detonation wave in compact NSTEX composition 5) Transmission and detonation of the secondary PETN charge [1]

Nanothermites exhibit high flame propagation velocities only in the loose powdery state. This is due to poor convection of the hot gases when the material is denser, owing to reduced internal porosity. This effect was identified by Prentice et al in Al/WO3 nanothermite[19] and is attributed to the melt dispersion mechanism of Aluminium, which occurs as a consequence of compressing the composition and leads to a slower rate of combustion[20,21]. Porous nanothermites are insensitive to friction, impact and electrostatic discharge and can be sawn or drilled without activating combustion. Upon ignition, nanothermites undergo rapid combustion wherein aluminium phosphate reduces to phosphorus, which then burns in contact with atmospheric oxygen[3].

One of the most suitable methods for the preparation of these porous nanothermites was proposed by Comet et al., who employed a chemical foaming method for the production of highly porous aluminothermic composition[22,23]. This is a two-stage exothermic process, where excess aluminium nanopowder is introduced into an aluminothermic mixture(Al/WO3) with aqueous orthophosphoric acid(H3PO4) solution. Although phosphate is inert in pyrotechnic applications, it exhibits an oxidative tendency at higher temperatures, especially in conjunction with aluminium nanopowders[18]. Before oxidising the aluminium core, the acid solution first reacts with the oxide shell of the nanoparticle. The by-products of the reaction also play a crucial role in the morphology and quality of the product, as the hydrogen gas and water vapour released during this reaction help in ensuring the porosity of the foam, while Aluminium phosphate(AlPO4) acts as a strong binder[23]. However, extreme care has to be taken during this process due to the risk of hydrogen explosion of fine aluminium powders and inorganic acid pastes such as phosphoric acid and sulphuric acid.

Despite numerous attempts, coating propulsive powders with thin porous nanothermites has proved to be quite challenging. Ensuring low density and high porosity of the nanothermite layer has been the biggest obstacle in engineering macroscopic NSTEX materials. Since most methods deposit nanothermite layers of high density, the propagation velocity of these composites has not been as high as expected[24].

3. Conclusion

Micron-sized metals have been profusely employed in pyrotechnics and explosives despite their negative impact on the environment. In addition, these materials have high ignition temperatures, low burning rates and correspondingly, low energy release rates. However, in the nano size, these particles exhibit size-dependent properties that are substantially different from their properties in the micron-size. These materials offer a green alternative to the currently available materials and have high intrinsic performance, attributed to their higher specific surface area and energy. Although nanomaterials have been present for a long time in the form of black powder and dynamite, their integration into operational systems is still premature and requires more academic and applied research.

The physicochemical properties of metal nanoparticles have shown evidence of being extremely useful. These properties can be further tuned by adjusting the size and porosity of these particles. Extensive research has led to the discovery, stabilisation and commercialisation of fine aluminium nanopowders, which is an invaluable component of energetic nanoparticle studies. The development of SFE by Comet et al. was a major breakthrough in manufacturing industry-compatible fine and ultrafine high-explosive nanopowders.

These explosive nanopowders, when mixed with nanothermites, form a highly advantageous composite that has similar properties to primary explosives while being benign and having tunable detonation velocity, which can be adjusted by varying the composition and porosity. However, despite the leap in efficiency, these metastable loose nanopowders are yet to be integrated into pyrotechnics and explosives as porous, solid composite mixtures. Development in this area of manufacturing macro-level systems with NSTEX could result in a significant leap in explosive and pyrotechnic efficiency, safety and sustainability.

List of abbreviations

SFE: Spray Flash Evaporation

NSTEX: Nano-Structured Thermites and Explosives

NS3E: Nanomaterials for systems under extreme stress

TNT: Trinitrotoluene

RDX: Hexogen

HMX: Octogen

PETN: Pentaerythritol tetranitrate

ADN: Ammonium dinitramide

CL-20: Hexanitrohexaazaisowurtzitane

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