*Prayogik Rasayan*

# Recent Progress in Nanothermite Materials: Fabrication, Reactivity, and Energetic Material Applications

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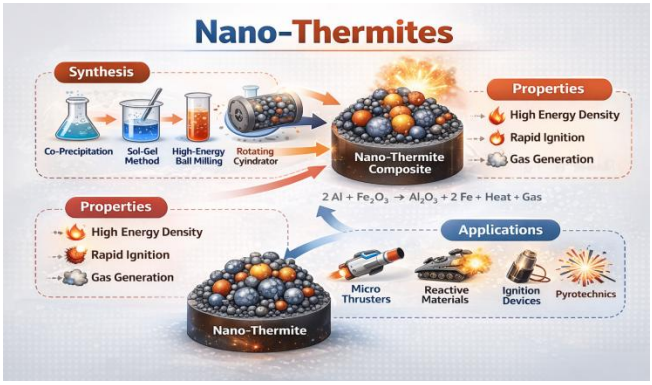
## Abstract

Thermite reactions between metallic fuels and oxidizers are highly exothermic and self-propagating, making them useful for applications ranging from pyrotechnics and devastation to thermal batteries, microactuators, and materials synthesis. Although aluminium-based thermites have been extensively studied, boron-based formulations deserve greater attention because boron offers superior volumetric and gravimetric energy densities, providing clear thermodynamic advantages. This paper surveys promising fuel candidates for thermitic compositions and reviews their potential roles in advanced energetic systems and high-energy materials technologies. It also evaluates the effects of nanoscale structuring on sensitivity and performance compared to micron-scale counterparts, and critically discusses the practical limitations and safety considerations associated with using nanoparticles in these contexts.

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## 1. Introduction

In recent years, nanothermites have attracted significant attention in the field of energetic materials because of their exceptional reactivity and energy-release characteristics. These materials consist of fuel and oxidizer components that are either intimately mixed at the nanoscale or chemically integrated into single-phase energetic systems. Such formulations are widely explored for applications in propellants, explosives, pyrotechnics, thermal batteries, micro electromechanical devices, and advanced material processing.

The origin of thermite chemistry dates back to the pioneering work of Hans Goldschmidt, who first reported thermite reactions in 1893 and later patented the process in 1895. Conventional thermite systems generally involve reactions between a metal fuel and a metal or non-metal oxide oxidizer, producing highly exothermic and self-sustaining reactions. These characteristics have enabled their long-standing use in welding, demolition, ignition devices, and heat-generating applications.

The development of nanothermites has further expanded the potential of thermitic materials. By reducing both fuel and oxidizer particles to the nanoscale, the contact area between reactants increases substantially, leading to faster ignition and accelerated reaction kinetics. Compared with traditional micron-sized thermites, nanothermites exhibit enhanced reactivity, rapid combustion behaviour, and improved effective energy output. This improved performance primarily arises from the transition of the reaction mechanism from diffusion-controlled processes to kinetically dominated regimes at nanoscale dimensions. [1–11]

Solid propellants, housed within the combustion chamber of a solid rocket motor, serve as the primary propulsion source for launch vehicles, spacecraft, missiles,

and related systems.[12] The selection of a specific propellant formulation is therefore tailored to the performance and operational constraints of each application. [13] Boron-rich fuels have historically been preferential for fuel-rich ramjet applications in medium to long-range air-to-air missiles, as their high energy per unit volume enables compact systems capable of extended range and higher speeds. Boron is particularly attractive as a high-energy metallic fuel due to its exceptional gravimetric (≈58.23 MJ $kg^{-1}$) and volumetric (≈136.38 kJ $cm^{-3}$) heat release upon combustion. [14] However, practical use of boron in propellant systems is hindered by ignition and combustion challenges: boron's high melting and boiling points increase its ignition threshold, and the rapid formation of a refractory boron oxide passivation layer on particle surfaces significantly suppresses reactivity and delays heat release (Figure 1). [15] To address these limitations, considerable research has focused on surface engineering approaches most notably the application of nanometre-scale transition metal oxide coatings and the development of boron-based nanocomposite thermites which promote oxide disruption, lower effective ignition temperatures, and enhance the rate and completeness of combustion. [16]

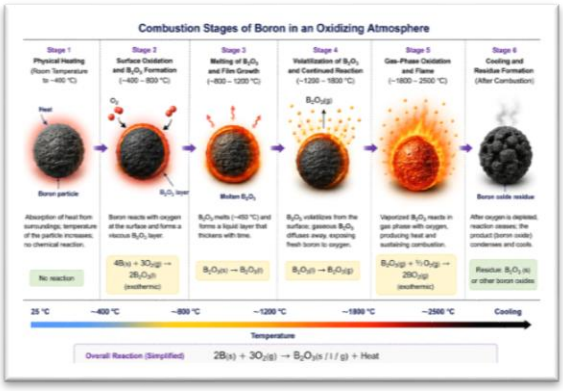


Figure 1. Various stages of Boron combustion

Traditional thermites are often used as energetic additives to increase the energy output of propellants, explosives, and pyrotechnic formulations. [17] The fundamental thermitic process is an oxidation-reduction reaction in which a metallic fuel (F) is oxidized by oxygen supplied from a metal oxide oxidizer (Ox), producing an oxide of the fuel and a reduced metal from the oxidizer. The reaction can be represented in generic form as,

$$MxOy + y\,Al \longrightarrow x\,M + y/2\,Al_2O_3 + Heat$$

Where MxOy denotes the metal oxide, M is reduced metal produced. Aluminium acts as a reducing agent. The thermite reaction releases substantial heat through redox conversion of the oxidizer and fuel. Nano composite thermites are an advanced class of energetic materials in which both oxidizer and fuel are engineered at the nanoscale. In these systems, reactivity is governed by interfacial and nanoscale chemical interactions, including increased contact area, reduced diffusion paths, and modified reaction kinetics rather than by the macroscopic mass-transfer limitations that control conventional, micron-sized thermites.

Nanoscale particles typically consisting of around $10^3$ atoms or fewer have a disproportionately large fraction of atoms at or near their surface. This high surface-to-volume ratio imparts properties that differ significantly from those of bulk or micron-sized counterparts. In particular, nano materials possess much greater specific surface area and show size-dependent reductions in melting and phase-transition temperatures. The increased interfacial area raises the number of reactive sites and shortens transport distances for reactants, thereby accelerating heterogeneous reactions, while the lowered melting and softening temperatures reduce ignition thresholds and enable earlier onset of combustion. These combined effects underpin the distinct thermochemical and kinetic behavior of nanoscale energetic components.

**Classification of energetic materials**

**Monomolecular energetic materials**

Monomolecular energetic materials are single molecular compounds in which energy is stored within the chemical bonds of the molecule itself; canonical examples include nitroglycerin (NG), 2,4,6-trinitrotoluene (TNT), cyclotrimethylene-trinitramine (RDX), cyclotetramethylene-tetranitramine (HMX), hexanitrohexaazaisowurtzitane (CL-20), and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). By contrast, formulations such as hydroxy-terminated polybutadiene (HTPB), ammonium perchlorate (AP), and ammonium nitrate (AN) are functional components used in composite propellants and oxidizer systems rather than monomolecular explosives: HTPB commonly serves as a polymeric binder/fuel, while AP and AN are ionic oxidizers. Although monomolecular compounds typically deliver rapid and well-defined energetic output, their practical use is constrained by trade-offs among energy density, sensitivity, and thermal or mechanical stability. These limitations have motivated the development of composite approaches, including nanostructured thermites and other engineered energetic composites, which aim to combine high energy release with controllable sensitivity and improved performance.

**2. Composite energetic materials**

Composite energetic materials (CEMs), or heterogeneous reactive materials, are intimate physical mixtures of metallic fuels such as aluminium, boron, magnesium, titanium, zirconium, silicon, and chromium with particulate oxidizers including CuO, $Fe_2O_3$, $Bi_2O_3$, and $WO_3$. Upon initiation, these mixtures undergo rapid oxidation-reduction reactions that convert chemical potential into thermal and mechanical output; reaction enthalpies are large, and peak reaction temperatures frequently exceed 3000K. The heterogeneous architecture of CEMs allows tailoring of energy release, burn rate, and sensitivity through control of particle identity, size, morphology, and mixing architecture, making them important in propellants, pyrotechnics, and specialized energetic systems.

Compared with monomolecular energetic compounds, composite energetic materials (CEMs) generally deliver greater combustion enthalpies and higher energy densities (see Table 1). A principal advantage of CEMs is the ability to tune their energetic and safety characteristics by selecting and engineering constituent particles fuel identity, oxidizer, particle size, and morphology enabling targeted

performance for diverse applications. A survey of the periodic table shows that only a limited subset of elements is practical as nanoscale metallic fuels. Fischer and Grubelich evaluated candidate fuels by calculating the heat released upon oxidation to their stable oxides and introduced a combined performance metric, the geometric mean of the mass and volume-based oxidation heats (i.e., the square root of their product) to rank intrinsic energy potential more objectively than either metric alone [18].

Table1. Critical review of fuels of potential interest for preparing nanothermites

| Fuels | Oxides | $Q_{exp}$ (kJ/g) | Criterion of interest (kJ/cm$^3$) | Drawbacks |
|---|---|---|---|---|
| Al | $Al_2O_3$ | 31.1 | 51.0 | -- |
| B | $B_2O_3$ | 59.0 | 90.2 | Reactive only at high temperatures |
| Be | BeO | 67.6 | 92.0 | Highly toxic, Carcinogen (category 1) |
| Hf | $HfO_2$ | 6.4 | 23.4 | Difficult to prepare in nano scale |
| La | $La_2O_3$ | 6.5 | 16.0 | Not Stable |
| Li | $Li_2O$ | 43.1 | 31.5 | Not Stable |
| Mg | MgO | 24.8 | 32.7 | Not Stable |
| Nd | $Nd_2O_3$ | 6.3 | 16.6 | Not Stable, ignition at low temperature |
| P(red) | $P_4O_{10}$ | 23.8 | 34.9 | -- |
| Si | $SiO_2$ | 32.4 | 49.5 | Reactive only at high temperatures or with strong oxidizers |
| Ta | $Ta_2O_5$ | 5.7 | 22.9 | Very expensive |
| Th | $ThO_2$ | 5.3 | 18.1 | Radioactive |
| Ti | $Ti_2O_3$ | 19.7 | 41.9 | Ignition at low temperature |
| Y | $Y_2O_3$ | 10.7 | 22.7 | -- |
| Zn | ZnO | 5.4 | 14.3 | Not Stable |
| Zr | $ZrO_2$ | 12.1 | 30.8 | Difficult to prepare in nano scale |

Fuels in energetic nanopowders exhibit effective densities that strongly depend on particle size, morphology, and packing arrangement; therefore, assessments of fuel performance must consider both mass-based and volume-based metrics. Although oxidation heat per unit mass is a straightforward indicator of energetic potential, the total energy available from a formulation is limited by the mass of fuel that can be loaded into a fixed volume. The combined criterion used in Table1 (the geometric mean of the mass- and volume-based oxidation heats) thus provides a more representative measure of practical energy output. Thermochemical ranking using this approach identifies beryllium, boron, aluminium, and titanium as the most promising metallic fuels for nanothermites; however, beryllium's acute toxicity and carcinogenicity make it impractical for most applications, as reaction products would be emitted as respirable particulates. Similarly, although boron has excellent theoretical gravimetric and volumetric energy metrics, its real-world reactivity in formulations is often compromised by surface oxide layers, agglomeration, and ignition or combustion limitations, resulting in performance below ideal predictions.

Yeh and Kuo reported that the combustion of micrometre-sized boron particles (2–3μm) occurs in two distinct stages. In the first stage, the particle burns while still encased in its native oxide layer; this process continues until the molten $(BO)_n$ phase, formed by the reaction of $B_2O_3$ with boron during heating, fully vaporizes and the boron core reaches its melting point of 2450K. The second stage involves the complete combustion of the exposed boron core, which may be controlled either by oxygen diffusion or by chemical kinetics: oxygen diffusion dominates for larger particles at elevated pressures, whereas kinetic effects govern the combustion of smaller particles at lower pressures. [19]

In a complementary study, Young et al. examined primary boron nanoparticles aggregated into sub-micrometer clusters. They found that, as with larger particles, combustion occurs in two consecutive stages. The ignition time of the nanoparticles decreases with increasing temperature, while oxygen concentration has minimal influence on ignition. However, oxygen levels strongly affect the combustion process itself, particularly at lower flame temperatures. Notably, the combustion duration of boron nanoparticles is not limited by diffusion or chemical kinetics. Young et al. concluded that heat dissipation in sub-micrometer boron clusters impedes melting, necessitating higher flame temperatures to achieve complete combustion. [20]

The full energetic potential of boron nanopowder is realized only when it is incorporated into formulations that maintain flame temperatures high enough to vaporize the surface oxide and melt the boron core. For example, Sullivan et al., reported that incorporating boron nanopowder (mean primary particle diameter ≈62nm) into an Al/CuOnanothermite measurably increased reactivity.[21] In contrast, titanium nanopowder exhibits very low ignition thresholds (around 100–200 °C), which poses handling and safety concerns at scale. Among candidate metallic fuels for nanothermites, aluminium remains the most practical: aluminiumnanopowders form highly reactive, adaptable composites with a wide range of oxidizers, can be rendered stable through appropriate passivation, present relatively low toxicity compared with other metallic fuels, and are available in large quantities from industrial production.

Zirconium and hafnium, although thermochemically attractive, present significant challenges for nanopowder production due to their very high boiling points and the demanding synthesis conditions required. More generally, many metals are inherently difficult to stabilize as nanopowders for fabrication or long-term storage. The temporal stability of metallic nanopowders is largely determined by the physicochemical properties of the native oxide layer that forms on each particle: a coherent, adherent, and dense oxide can passivate the surface and slow further oxidation, whereas a porous, cracked, or poorly adherent film allows ongoing corrosion. Continuous oxidation progressively

reduces the metal-to-oxide ratio and, in severe cases, the exothermicity of the oxidation process can accumulate to the point of self-heating or spontaneous ignition. Therefore, controlling the structure and integrity of the oxide is critical for the safe handling and reliable performance of metallic nanopowders in energetic applications.

Metal nanopowders pose a higher pyrophoric risk because their large specific surface area accelerates heat generation, while limited thermal conduction hinders heat removal, leading to rapid temperature rise. To reduce ignition hazards, best practices include storing nanopowders in small batches (typically gram-scale), minimizing exposure to oxidizing atmospheres, and using conductive (metallic) containers to improve heat dissipation and reduce electrostatic accumulation. Container geometry should be chosen to maximize packing density and thereby reduce the proportion of surface area exposed to oxidants. Additionally, inert-atmosphere packaging, proper grounding and bonding to prevent static discharge and strict handling protocols (controlled transfer, limited agitation, and rigorous housekeeping) further reduce the likelihood of accidental ignition during storage and processing.

Fischer's classification omits zinc as a viable thermitic fuel, likely because its thermo chemical properties are less favorable for high-energy redox reactions. Zinc's relatively low boiling point (≈907°C) facilitates vaporization and the production of nanoscale particles, yet empirically, zinc shows limited reactivity with common oxidizers such as CuO and $Bi_2O_3$ compared with aluminium. This subdued behavior likely reflects a surface-limited interaction in which zinc vapour reacts primarily at the oxide interface to form a ZnO shell; that shell subsequently impedes further transport of zinc vapour to the unreacted oxide core, curtailing the reaction's progression. Moreover, sub-micrometre zinc powders are prone to rapid atmospheric aging, further restricting their practical utility in nanothermitic compositions.

Protracted observations of a commercial zinc nanopowder, which was stored in a sealed glass container for thirty months, documented significant aging effects. Initially, the zinc particles possessed a well-defined, spherical, and faceted morphology. However, over the storage period, the particle surfaces developed a zinc oxide (ZnO) coating. This led to the gradual loss of the initial morphology and subsequently promoted agglomeration into larger clusters. This evolution underscores the susceptibility of sub-micrometer zinc powders to oxidation and morphological degradation during storage, even under nominally sealed conditions.

Silicon and red phosphorus are metalloids of interest for nanothermite formulations, although they are not included in Fischer's classification. Porous silicon, when combined with strong oxidizers such as metal perchlorates, produces rapidly deflagrating compositions, primarily due to its high surface area and reactive surface chemistry. Strictly speaking, these systems differ from classical thermites because they contain only minor metallic fractions that do not serve as the principal fuel in the redox reaction; instead, porous silicon often acts as a performance-enhancing additive within aluminothermic or other metal based mixtures. Similarly, red phosphorus forms combustible mixtures with certain metal oxides and can provide substantial reactivity when incorporated as sub-micrometre particles, which further accelerates reaction rates and increases energy release in these formulations [22–27].

**3. Aluminum Nanopowder: A key Material for Nanothermites**

The historical development of thermitic reactions are closely linked to advances in aluminium production. The ability to manufacture aluminium on an industrial scale in the late nineteenth century made aluminothermic formulations practicable, and Hans Goldschmidt's 1895 patent formalized their use for producing metals, metalloids, and alloys. Traditionally, micrometer-scale thermites found civilian applications such as rail welding and steel cutting, while their military use was largely limited to incendiary charges and flare compositions. Over the past two decades, substantial progress in the industrial synthesis of aluminiumnanopowder (nominally 50–200nm) has made these materials widely available and has driven renewed academic and technological interest in nanothermites [28].

**On the Safe Handling of Aluminum Nanopowders**

Handling aluminium nanopowders requires stringent precautions due to their pyrophoric potential and unresolved toxicological concerns. Although bulk aluminium is not acutely toxic, nanoscale aluminium presents distinct exposure risks that are rarely addressed in the literature; some studies have suggested associations between aluminium exposure and long-term health outcomes, including autoimmune and neurodegenerative conditions, which warrant cautious interpretation and further investigation. Researchers should therefore adopt conservative safety practices when working with aluminiumnanopowders, prioritizing engineering controls (local exhaust ventilation, inert-atmosphere glove boxes), administrative controls (small-batch handling, restricted access, standard operating procedures), and appropriate personal protective equipment (respiratory protection, antistatic garments, and eye protection). Inhalation is the principal route of occupational exposure for nanoparticles, whereas intact skin provides a substantial barrier to penetration; therefore, measures that minimize airborne release and ensure effective respiratory protection are particularly important to reduce both acute pyrophoric risk and potential chronic exposure [29].

When handling aluminiumnanopowders, insulating gloves and contact with dielectric surfaces (e.g., borosilicate glass) can promote electrostatic charging and unintended dispersion of fine particles; therefore, personnel should avoid procedures that increase turboelectric generation and particle aerosolization. Work should be carried out using conductive, grounded tools and containment (e.g., grounded metal tweezers, antistatic mats, or inert-atmosphere enclosures) to reduce static accumulation and airborne release. Surfaces contaminated with nanopowder should be cleaned promptly with wet absorbent towels or wipes containing a mild surfactant to capture and remove particulates effectively; dry sweeping or compressed-air cleaning is contraindicated as it redistributes particles into the air.

Aluminium nanoparticles readily adhere to porous materials, both on surfaces and within bulk matrices. For example, when a sponge is used to clean nano-Al powder, complete removal remains difficult even after several cycles of wetting and wringing. Although the sponge may appear visibly

contaminated, washing with a surfactant effectively removes most trapped nanoparticles. Therefore, liquid detergents should always be used when cleaning objects that have been in contact with aluminiumnanopowder to ensure thorough decontamination. In the event of accidental skin contact, rubbing with a towel is strongly discouraged, as this can embed nanoparticles into pores. The recommended procedure is to gently shake off loose powder under an extractor hood, then carefully wash the affected area with cold water and liquid soap to remove residual contamination safely.

Aluminiumnanopowders consist of discrete nanoparticles that naturally agglomerate into micrometer-scale clusters due to interparticle surface forces. This tendency reduces the proportion of material likely to become airborne during careful handling. Nevertheless, operations involving nano-Al should be carried out under a well-functioning fume hood or extraction system to minimize inhalation exposure to free nanoparticles. When aerosolized, these fine particles generally follow the bulk airflow, although individual nanoparticles can display unpredictable, Brownian-like trajectories due to their small mass and high surface-area-to-volume ratio.

Respiratory protection is essential when working with aluminiumnanopowder; well-fitting half-mask respirators equipped with high-efficiency particulate filters (e.g. FFP3) are recommended, as the multi-layer structure and depth filtration mechanisms trap most airborne nanoparticles despite their small size. The highest level of control is provided by an inert-atmosphere glove box, which prevents atmospheric dispersion of nano-Al and is strongly advised for synthesis, weighing, and large-scale handling. Engineering controls (local exhaust ventilation, grounded conductive tools, anti static mats) and administrative measures (small-batch processing, restricted access, written procedures) further reduce release and exposure. As aluminiumnanopowder is a finely divided fuel that ignites more readily and reacts more rapidly than micron-scale aluminium, precautions to avoid forming airborne nano-Al/air mixtures are critical: such aerosols present a substantial dust-explosion and pyrophoric hazard. Therefore, avoid dry sweeping or use of insulating gloves that promote turboelectric charging, prefer wet or surfactant-assisted cleanup, ensure effective grounding and bonding, and employ intrinsically safe handling practices (inerting, controlled transfer, minimal agitation). These combined measures mitigate both the acute pyrotechnic risks and the potential for chronic inhalation exposure associated with nanoscale aluminium.

Aluminiumnanopowder displays marked reactivity with oxygen-bearing species, enabling various combustion and propulsion applications. Dispersion of nano-Al in liquid or frozen water commonly known as ALICE (Aluminium–Ice) propellants have been studied for rocket propulsion and tested in experimental motors, where the aluminium-water reaction generates hydrogen gas that significantly contributes to the propulsive energy release. These systems demonstrate the potential of nano-Al to increase specific energy, but their extreme reactivity imposes strict requirements on formulation, handling, and storage to manage risks. Similarly, nano-Al reacts vigorously with mineral acids; for example, pastes of aluminiumnanopowder and sulphuric acid can produce hydrogen detonations if exposed to ignition sources. These characteristics highlight both the technological potential of aluminiumnanopowders in energetic applications and the necessity for rigorous safety controls during their use. [30, 31]

The vigorous reactivity of aluminiumnanopowder with acids depends strongly on acid concentration and formulation. For example, the highly exothermic reaction between nano-Al and ortho-phosphoric acid ($H_3PO_4$) can be moderated by diluting the acid with water; dilution reduces the rate of hydrogen generation and the peak heat release. In contrast, removing water from $H_3PO_4$ with a dehydrating agent such as phosphorus pentoxide ($P_2O_5$) can concentrate the exotherm sufficiently to ignite the mixture and provoke a hydrogen gas explosion. Nano-Al also reacts vigorously with hydrochloric acid (HCl) solutions, producing hydrogen and heat; therefore, contact between aluminiumnanopowder and aqueous mineral acids must be avoided or managed under strictly controlled conditions with appropriate inerting and ventilation to prevent fire, detonation, or toxic exposure [32].

When aluminiumnanopowder comes into contact with aqueous acids, it undergoes a characteristic two-stage reaction. An initial induction period occurs as the acidic medium penetrates the native oxide shell and reaches the aluminium core; once the core is exposed, oxidation accelerates and the system enters a runaway stage in which a rapid exothermic reaction causes local boiling and a marked rise in temperature. The increased temperature reduces the solubility of hydrogen chloride and promotes its rapid release, while simultaneous evaporation of water and evolution of hydrogen amplify the pressure build-up. The swift generation of multiple gaseous species can produce pressure-driven (pneumatic) explosions; although the presence of non-combustible vapours ($H_2O$, HCl) tends to inhibit immediate ignition compared with pure hydrogen, successive hydrogen deflagrations remain possible if an ignition source is present. Therefore, contact between aluminium nanopowder and aqueous acids should be avoided except under strictly controlled laboratory conditions and in minimal quantities, as nanopowder-acid mixtures pose substantially greater hazards than analogous systems containing micrometer-scale aluminium.

Aluminium nanopowders react vigorously with alkaline solutions (e.g., NaOH, KOH), producing hydrogen and soluble aluminate species; the induction period is typically short, and reaction rates increase markedly with temperature. Under conditions of hydroxide excess, aluminium is consumed quantitatively as aluminate ions, a reaction that can be exploited to deactivate or neutralize many nanothermite formulations by reactive dissolution of the metallic fuel. Because the process liberates flammable hydrogen, neutralization must be performed with strict controls: conduct the operation in a well-ventilated fume hood or under local exhaust ventilation, add the nanothermite incrementally in small portions, allow each addition to complete before adding more, and avoid confinement or ignition sources that could permit accumulation of an explosive atmosphere. Critically, this dissolution protocol must not be applied to compositions that generate oxidizing gases or release oxygen on contact with alkali (e.g., persulphate-containing mixtures), since such

combinations can produce highly hazardous redox environments. [33]

Aluminium nanopowders are susceptible to ignition by low-energy, high-power stimuli such as electrostatic discharges or photographic flashes. The transient thermal impulse produced by a photo flash can raise surface temperatures by several hundred degrees Celsius with heating rates on the order of $10^6$ °C $s^{-1}$, promoting ignition. This vulnerability is not unique to aluminium; other dark, combustible nanopowders in a loosely packed state (e.g., carbon nanotubes, boron, titanium) and energetic formulations containing them exhibit similar behavior. The underlying mechanism is largely thermal-confinement at the particle surface poor thermal conduction prevents rapid dissipation of the absorbed energy into the bulk, causing localized overheating and ignition. Because the incident heat flux from a flash decays approximately with the square of the distance from the bulb, photographic flashes can still pose a serious ignition hazard and should be avoided when handling or imaging samples of aluminium nanopowder. [34]

**Synthesis Methodology**

Three principal methods are used to prepare nanothermites: arrested reactive milling, physical (top-down) mixing, and sol–gel synthesis. These approaches enable access to nanoscale particle sizes and offer varying degrees of intimate contact between fuel and oxidizer. Arrested reactive milling produces intimately mixed nanoscale domains by mechanically activating and then quenching the reaction. Physical mixing combines separately synthesized nanopowders to control composition and particle morphology, generally providing less interfacial intimacy. Sol-gel routes form oxide matrices that encapsulate or disperse fuel nanoparticles, yielding homogeneous microstructures with tunable porosity and contact area. Transitioning from micron to nanoscale fabrication therefore permits tailored control over particle size, interface architecture, and reaction coupling, which in turn strongly influences ignition, propagation, and overall energetic performance.

Arrested reactive milling (ARM) is a mechanical synthesis route for nanoenergetic composites in which metal oxide and aluminium powders are co-milled in a ball or shaker mill. Although the final particulate dimensions may remain in the micrometer range, ARM produces nanoscale interleaving of fuel and oxidizer, typically layered domains on the order of 10-100nm, so that the resulting composites exhibit reaction behavior characteristic of nanothermites. Typical product particles range from ~1 to 50 μm, and their morphology and degree of intermixing are controlled principally by milling duration and the choice of milling media. Extended milling increases intimacy of contact but, beyond a critical size/time threshold determined by initial particle sizes, media, and oxide identity, mechanically induced reactions can ignite the charge; consequently, liquid solvents (e.g., hexane) are commonly employed to suppress static charging and dissipate heat, and milling is intentionally terminated before self-ignition occurs, hence the term “arrested” reactive milling. Key advantages of ARM include near-theoretical compaction of particles, encapsulation of aluminium within a dense particle matrix that reduces the influence of inert alumina, the ability to use non-nanoscale precursors, and facile control of reactivity via milling time. Its principal limitation is sensitivity: many termite combinations ignite prematurely under the mechanical and thermal stresses of milling, restricting the scope of compositions accessible by this technique. [35, 36]

Sol-gel methods exploit the structural and compositional control offered by sol-gel chemistry to produce nanothermitic composites with highly engineered fuel-oxidizer interfaces. In these formulations, aluminium nanoparticles are embedded within the pore network of a metal-oxide matrix, which markedly reduces diffusion distances and increases interfacial contact area compared with physically mixed powders, thereby enhancing reaction coupling and effective power. Typical syntheses introduce a suspension of aluminium nanopowder into a metal oxide solution immediately before gelation; subsequent drying and processing yield xerogels or aerogels that retain tailored pore architecture. Sol-gel processing enables precise control of interfacial area, pore size distribution, and matrix geometry, and permits incorporation of organic additives that act as gas-forming agents to modify burn behavior. [37-41] Additional advantages include the ability to fabricate low-density aerogel or xerogel morphologies and energetic surface coatings [43]. A notable drawback is the risk of premature oxidation of aluminium nanoparticles by residual water in the gel network before solvent removal; this can be mitigated by preparing oxide precursors by sol-gel methods followed by post-drying physical mixing with aluminium, although this approach sacrifices some of the superior interface intimacy achievable by in situ incorporation. [44]

**Applications**

The tunable properties of nanothermites enable a broad and growing range of potential applications. Their energy densities comparable in some cases to those of lithium based batteries have motivated exploration of power-generation and propulsion uses, including micro scale thrusters, energetic surface coatings, and nanoscale welding. The pronounced pyrotechnic behavior of nanothermites also makes them candidates for gas-generation systems (e.g., automobile airbags), impact-activated warheads, environmentally friendlier ammunition primers, electric initiators, and even, in the case of the most rapid formulations, primary explosive roles. While many application concepts remain at the proposal stage, experimental work to date notably on micro scale propulsion, primers, and electric igniters, has produced encouraging results. [38, 42, 45–55]

Micro scale propulsion, often termed micro pyrotechnics or micro-energetics, concerns the generation of thrust at dimensions below 1mm and finds use in rapid actuation and propulsion for small spacecraft. Conventional macroscopic energetic materials (e.g., RDX or HMX) are poorly suited to such scales because combustion propagation within sub-millimeter geometries is quenched by excessive heat losses to the confinement, preventing sustained reaction. Nanothermites, by contrast, offer substantially higher effective energy densities and much faster reaction coupling, so that heat losses to the combustion chamber become comparatively

negligible and self-sustaining propagation is achievable in micro scale devices. [47, 56].

An ammunition primer is the component of a cartridge that is struck by the firearm's firing pin to initiate propellant combustion. Conventional primers have traditionally employed lead-based primary explosives (e.g., lead azide, lead styphnate) because these compounds reliably detonate under mechanical impact and generate the hot gases and flame necessary to ignite the main propellant charge. However, the toxicity and environmental persistence of lead salts present significant health and ecological concerns. Consequently, nanothermitic formulations have been investigated as candidate lead-free alternatives; by tuning composition, particle size, and microstructure, researchers have produced nanothermites with sensitivity and output characteristics analogous to conventional primer mixtures, offering a potential path to reduce lead exposure from small-arms ammunition. [37. 42, 57]

Electric igniters, commonly known as electric matches, are widely used in propellant, explosive, and pyrotechnic systems wherever initiation by electrical current is required. They provide precise timing for the initiation of devices ranging from small rocket motors to blasting caps and large-scale firework arrays. A typical electric igniter consists of a resistive bridge wire embedded beneath a pyrotechnic head; when a predetermined current passes through the bridge wire, the resulting Joule heating ignites the surrounding composition. Conventional electric match formulations often incorporate toxic lead compounds (e.g., lead tetroxide, lead thiocyanate, lead nitroresorcinate), prompting the search for environmentally benign alternatives. Nanothermitic compositions have emerged as promising lead-free candidates, as their sensitivity, ignition characteristics, and thermal output can be engineered to match or exceed those of traditional primer and match materials while eliminating lead-based ingredients [42, 54].

**Sensitivity**

An ideal energetic material achieves a balance of high performance and thermal stability while displaying low sensitivity to accidental initiation. Nano-crystallization has attracted interest as a potential route to reduce sensitivity: both theoretical models and experimental studies suggest that decreasing crystallite size can lower impact sensitivity by reducing defect populations (e.g., inclusions, dislocations, and grain-boundary networks) within individual particles. Nevertheless, many reported experimental reductions in impact sensitivity suffer from limited statistical power, and further rigorous studies are required to confirm a general trend. Conflicting results have also been observed: shock sensitivity correlates strongly with particle quality, such that particles with higher average density, and therefore fewer voids and inclusions typically demand greater shock pressures to initiate. Particle morphology likewise affects sensitivity, indicating that size, internal defect structure, density, and shape must all be considered together when assessing whether nano-crystallization will reduce or exacerbate an EM's sensitivity. [58–62]

Formulations, rather than pure energetic compounds, are typically used in practical systems, with the energetic ingredient blended into matrices containing polymeric binders (such as waxes, paraffin, or elastomeric binders), curing agents, plasticizers, catalysts, stabilizers, burn-rate modifiers, and metal additives. These ancillary components are selected to tune mechanical, thermal, and ballistic properties, as well as to moderate sensitivity and processing behavior. Nano-crystallization of energetic phases is attractive because reduced particle size can lower intrinsic sensitivity, but incorporating energetic nano materials into formulations presents processing challenges: particle size strongly influences slurry rheology, mixing behavior, and castability in propellant and plastic-bonded explosive systems. Consequently, the net benefit of using nano-crystalline energetic ingredients depends on the formulation, and whether they provide superior propellant or explosive performance compared to conventional micron-scale materials must be evaluated on a case-by-case basis.

Nanoscale reduction of particle size affects not only sensitivity but also phase transition and decomposition temperatures. As particle dimensions decrease, the proportion of surface atoms or molecules increases, and surface species have fewer nearest neighbours and weaker cohesive forces than bulk species. This reduction in surface binding energy lowers the effective melting and decomposition temperatures of nanoscale materials compared to their micron-sized counterparts, an effect that scales with specific surface area and becomes pronounced as particles approach the nanometer scale.

Numerous studies report the synthesis and characterization of nanoparticles of both energetic and inert materials using various techniques, including spray drying, electrospray, sol-gel processing, mechanical milling, anti-solvent precipitation, and hydrothermal synthesis. These demonstrations confirm that energetic nanoparticles can be fabricated by multiple methods. [59,63–68] Critical questions remain regarding process scale-up and whether composite nano materials provide superior overall performance compared with analogous micron-scale composites. Wet processing routes, such as sol-gel and anti-solvent methods, offer intrinsic safety advantages because the reactive constituents are dispersed in solvent during synthesis. This permits larger-scale production with reduced pyrophoric risk and enables safe intermediate storage prior to final drying and deployment. [59,65] For example, Bayat and Zeynali applied anti-solvent precipitation to produce nano-HMX, illustrating the potential of solution-phase approaches to generate energetic nanoparticles under safer processing conditions. Ultimately, the suitability of any production method must be judged on its ability to deliver reproducible material properties, economically viable throughput, and demonstrable performance gains at application scale.

Nano-sized aluminium has long been incorporated into energetic formulations and has been shown to enhance propellant burning rates, particularly in systems containing oxidizers with a positive oxygen balance. As particle dimensions decrease, the specific surface area increases, improving intimate contact with oxidizing species and thereby accelerating combustion kinetics. However, most contemporary research on energetic nano materials remains concentrated on the synthesis and physicochemical characterization of single component nanoparticles; comparatively few studies have addressed the integration of

these nano materials into formulated propellants or explosive compositions and the resulting performance at the systems level. [65, 69–77]

Zhaohu Liu et al. report a ternary nanothermitic system of aluminium, $MnO_2$, and CuO, showing that mixed oxidants substantially modify key reaction metrics. They demonstrate that adjusting oxidant composition changes ignition delay, flame temperature, burning rate, and peak pressure. The ternary formulation enhances flame intensity and raises combustion temperatures compared to binary systems. These findings suggest that deliberately combining oxidizers enables tailored thermal output and dynamic response in nanothermitic formulations. [77]

Yuxiang Li et al. mixed Al/CuO nanothermites with a nitrogen-rich additive (TACP), showing that the new mix makes more gas, creates higher peak pressure, and requires less heat to start and decompose. Adding the nitrogen-rich compound boosts gas production and changes how the nanothermite responds to heat, resulting in stronger pressure output and easier ignition than plain Al/CuO. [72]

Chen et al. investigated the effect of incorporating a poly(vinylidene fluoride) (PVDF) binder into nanothermitic formulations and found that binder content substantially modifies the reaction pathway, ignition threshold, and combustion rate. Their results show that increasing PVDF fraction alters the temporal sequence of reaction stages, elevates or suppresses ignition sensitivity depending on composition and micro-structure, and measurably changes flame propagation velocity, indicating that binder loading is a critical parameter for tuning the thermal-reactive behavior of composite nanothermites. [73]

This study examines direct-write fabrication of Al/CuOnanothermites incorporating variable loadings of the fluoro-polymer binder Viton F2311, and demonstrates that increased binder content improves processability while accelerating combustion, producing flame temperatures in the order of 2400 K. Complementary work shows that the choice and concentration of additives, including different polymeric binders and fluorinated polymers, systematically modify energy release, burn rate, and sensitivity, providing a practical means to trade off performance against stability and safety in Al/CuOthermitic formulations. [74, 75]

Spitzer et al. demonstrated the production of nanoscale HMX via Spray Flash Evaporation (SFE). [78] The synthesized particles nominally ~100nm were characterized by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD), confirming the nanoscale morphology and crystalline phase. The authors further noted that the SFE approach is adaptable and could, in principle, be extended to synthesize other energetic nitro-compounds such as TNT, RDX, and CL-20, indicating the method's broader applicability for generating nano-sized energetic materials [72].

Jie Li et al. employed reactive molecular-dynamics simulations to investigate the thermal decomposition of HMX nanoparticles (≈30–70 Å). Their results indicate that both nanoscale structuring and elevated temperatures (~2000–3000K) markedly accelerate decomposition kinetics; the earliest bond scission event identified in these simulations is $N–NO_2$ cleavage, which initiates the decomposition cascade. [78-81]

Wu, Li, et al. synthesized spherical composite particles in which NTO forms a coating over HMX cores. These composites preserve the intrinsic energy content of HMX while simultaneously reducing mechanical sensitivity and enhancing thermal stability, demonstrating that surface functionalization with energetic coatings can effectively improve safety without compromising performance. [82]

Bayat and Zeynali prepared nanoscale HMX and CL-20 using an anti-solvent precipitation method, with particle characterization performed by SEM and XRD. Their studies examined key parameters influencing particle size and morphology, including surfactant type, anti-solvent temperature, compressed air flow rate, and nozzle diameter. In their 2011 study, the resulting nanoparticles were predominantly spherical or ellipsoidal, with an average diameter of approximately 95 nm, demonstrating the method's ability to produce uniform energetic nano-crystals. [59, 67]

Chen S. et al. employed core-shell architectures, surface coatings, and three-dimensional network composites to intimately integrate CL-20 with reactive aluminium (or Al-based nanothermite) in order to modulate sensitivity and combustion behaviour. Representative strategies include conformal aluminium or Al@Co coatings on CL-20 particles and embedding CL-20 within polymer/oxidizer matrices; these approaches preserve the explosive's energetic performance while reducing mechanical sensitivity and enabling tailored burn profiles. [60]

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Pang et al. synthesized nano-TATB using a solvent/non-solvent precipitation method. The resulting particles were predominantly spherical or ellipsoidal, with an average size of approximately 60 nm, and exhibited a tendency to agglomerate. Compared to micro-TATB, the nanoscale material displayed a lower thermal decomposition temperature, suggesting reduced stability under thermal stress due to the increased surface-to-volume ratio and the higher fraction of surface atoms. [73]

Qiao et al. reported the production of nanoscale NTO particles using a spray-freezing-into-liquid (SFL) technique. The resulting nanoparticles were elongated, with sizes ranging from 70 to 90 nm. Similar to observations with nano-TATB, the nano-NTO particles exhibited lower thermal decomposition temperatures compared with their micron-sized counterparts, indicating decreased thermal stability associated with the nanoscale dimensions. [74]

Wu et al. fabricated spherical composite micro-and nanoparticles with NTO coatings over HMX cores. These

composites retain the intrinsic energy of HMX while significantly reducing mechanical sensitivity and enhancing thermal stability. This demonstrates that surface coating with energetic materials can improve safety without sacrificing energetic performance. [82, 83, 84]

Castro Rosario et al. synthesized nanoscale RDX by directing an aerosol jet of RDX onto glass substrates. Following five exposures, SEM analysis identified approximately 130 discrete particles on the substrate, each with an average diameter of ~400nm. These results demonstrate the effectiveness of aerosol-based deposition for producing isolated energetic nanoparticles. [85]

Zhang et al. employed an electrospray technique to fabricate RDX particles encapsulated with a polymeric binder and integrated Al/$Fe_2O_3$nanothermitic components. The resulting core-shell particles exhibited improved combustion characteristics and a synergistic enhancement of energy release relative to physically blended mixtures, indicating that electrospray-mediated encapsulation can promote intimate fuel-oxidizer contact and more efficient reactive coupling in energetic composites. [86]

A combined experimental and computational study shows that Al/$MoO_3$nanothermite alters the thermal decomposition pathways of RDX and reduces its apparent activation energy. The authors attribute this to catalytic electron-transfer at the Al-RDX interface, supported by kinetic analysis and modeling. They highlight the role of close fuel-oxidizer interactions in modulating energetic material reactivity. [87]

Several groups have used electrospray and in situ deposition to form core–shell structures. In these, RDX cores receive conformal coatings of Al-based nanothermite shells (aluminium with various metal oxides). These constructs consistently ignite more rapidly, exhibit higher local combustion temperatures, and show systematic changes in mechanical and thermal sensitivity compared with physically mixed samples. Improved performance comes from the close, nanoscale contact between the explosive core and reactive shell. This enhances heat transfer and reactive coupling during initiation and decomposition. Core-shell designs offer a promising way to tailor energetic output and sensitivity. However, increased interfacial reactivity demands careful attention to handling and safety. [89-91]

Experimental studies show that incorporating aluminium and composite-oxide nanothermites into RDX formulations can modify detonation behavior. This approach can alter parameters such as the apparent activation energy and peak detonation pressure, enabling performance to be tuned to meet specific objectives. These hybrid mixtures enhance coupling between the high explosive and reactive metal-oxide phases. However, the resulting performance gains are accompanied by changes in sensitivity and handling hazards. Comprehensive sensitivity characterization (mechanical, thermal, and shock) and rigorous safety evaluation are required before such formulations can be considered for practical use. [89]

A 2024 experiment shows that adding certain chemicals to nanothermites, including common explosives, can allow for controlled gas release and adjusted burning behavior. The study explains how these materials are made and measures their gas output, burn speed, and temperature. It describes how changes in ingredients and production methods affect how the materials react and what they produce. These results help create RDX-nanothermite mixtures, offering clear advice on how to make these hybrids and set goals for their gas generation and burning properties. [90]

Li et al. synthesized nanoscale CL-20 via ball milling and characterized the products by scanning electron microscopy, which revealed pseudo-spherical particles with an average diameter of approximately 200 nm. Consistent with observations for other energetic nano-crystals (e.g., nano-TATB and nano-NTO), the nanoscale CL-20 exhibited a depressed thermal-decomposition peak relative to its micron-sized analogue, indicating reduced thermal stability associated with nanoscale dimensions. [66]

Electrostatic spraying has been used to fabricate CL-20 composite microspheres with narrow size distributions and controllable shell architectures. This technique permits the precise incorporation of energetic additives, including nanothermitic constituents, onto CL-20 cores, enabling engineered core-shell CL-20@Al/oxide constructs with finely tuned safety-performance trade-offs. The resulting microspheres offer tight control over shell thickness, composition, and homogeneity, making electrostatic spraying a promising route for designing energetically coupled, less-sensitive formulations with predictable ignition and combustion behavior. [91]

Poly(vinylidene fluoride) (PVDF) has been studied as both a binder and a complementary oxidizer to modulate the reactivity and safety profile of CL-20. Although the referenced study focuses on PVDF-functionalized CL-20 rather than a complete nanothermite formulation, the approach is directly relevant to CL-20/Aloxide hybrids because fluoro-polymers such as PVDF promote intimate interfacial contact with metallic fuels and allow tuning of the overall oxidative balance. Incorporation of PVDF can therefore serve dual roles, improving mechanical integrity and processing behavior while adjusting combustion pathways and gas-phase products, making it a valuable strategy for engineering safer, performance-optimized CL-20-based nanothermitic composites. [92]

Research into carbon nano materials (CNMs), including fullerenes, expanded graphite, carbon nanotubes (CNTs), graphene, and graphene oxide (GO), has expanded rapidly across energy storage, electronics, catalysis, biomaterials, and biomedical fields. A review by Si-Ping Pang et al. examined strategies for functionalizing CNMs with energetic moieties, thereby converting these materials into reactive additives. Functionalized fullerenes, CNTs, and GO are particularly attractive for incorporation into nanothermites, solid propellants, and gas-generation systems because they offer high surface area, facile chemical modification, and catalytic activity that can promote combustion chemistry and tailor reaction pathways. These attributes, together with scalable preparation methods, make CNM-based additives promising tools for tuning performance and reactivity in advanced energetic formulations. [93-96]

TATB and NTO are intrinsically low-sensitivity energetic compounds, and further reductions in their sensitivity may provide limited practical benefit compared to the complexity and risk introduced by additional processing. By contrast, CL-20 combines exceptionally high performance with increased sensitivity, making it a compelling candidate for nanoscale engineering. Downsizing CL-20 particles can potentially improve processability, enable novel composite architectures and when combined with suitable coatings or matrix materials, offer a way to reconcile its high energetic output with improved handling safety. Therefore, targeted nano-particulation of CL-20, together with surface modification or encapsulation strategies, represents a promising approach for achieving performance gains while mitigating sensitivity-related hazards.

Particle size influences the sensitivity of energetic materials, but the effect is often indirect. Reducing particle diameter decreases inter-particle void space and can lower the probability of structural defects (such as inclusions, dislocations, and voids) within individual crystals, both of which tend to increase initiation thresholds. Consequently, particle quality, determined by crystallization pathway and processing conditions, strongly governs sensitivity. Empirical studies comparing different synthesis and crystallization methods indicate that optimizing growth routes to produce dense, defect-poor particles is as important as absolute particle size for achieving reduced mechanical and shock sensitivity.

Methods for producing energetic nano materials are abundant in the literature, but their scalability remains a critical issue. Solvent-based processes offer inherent safety advantages because reactive constituents are dispersed in a liquid medium during synthesis; consequently, sol-gel and solvent/anti-solvent precipitation techniques, both of which operate in solution, are particularly promising candidates for scale-up. Evaluating these routes requires consideration of throughput, solvent recovery, process safety, and the maintenance of particle quality and morphology during larger-scale operation. However, their wet-processing nature makes them more amenable to safe, industrial implementation than many dry synthesis methods.

## 4. Conclusions

**Future Challenges**

The field of nanothermites confronts significant challenges that reside in both its theoretical foundation and its practical implementation. Although the research trajectory indicates sufficient progress for the near-term incorporation of nanothermites into propellant, explosive and pyrotechnic systems, a substantial number of proposed applications lack experimental validation, and the development of predictive models for nanothermitic reaction dynamics remains nascent. A challenge of equal priority is the necessity for comprehensive toxicological and environmental lifecycle analyses. The resultant occupational health, environmental impact, and long-term ecological outcomes associated with the synthesis, manipulation, and deployment of these energetic nanopowders are insufficiently characterized and must be systematically investigated in parallel with safety and performance metrics. These deficiencies necessitate coordinated efforts involving multi-scale computational modeling, standardized experimental methodologies, and interdisciplinary research coupling materials efficacy with risk assessment.

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