Review paper

Review of Nano-thermites: a Pathway to Enhanced Energetic Materials

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Abstract: Nano-thermites or metastable intermolecular composites (MICs) have been implemented into modern research on energetic materials as they offer much higher energy densities, higher rates of energy release, stability, and safety (lower sensitivity). This paper reviews several synthetic methods for MICs that have been well thought-out for energetic applications, advantages and disadvantages, as well as the characteristics of each manufacturing technique. The techniques presented include powder mixing, sol-gel, synthesis of MICs based on nano-porous silicon (Psi), sputtering, multilayer nano-foils and electrolytically plated carbon nano-materials for nano-thermite applications. These techniques offer enormously different characteristics and, through the variation of various chemical techniques and conditions, a wide range of chemical and energetic properties may be attained. This may give the opportunity for the safe use of MICs as replacements for some conventional energetic materials in various applications, and may also enable us to study the effects when incorporating these MICs into energetic matrixes, as a promising and feasible research field.

**Keywords:** energetic materials, nano-thermites, synthesis, applications

1 Introduction

Advanced weapon systems require the continuous development and enhancement of energetic materials with remarkable performance [1-3]. The investigation of energetic materials has been increased significantly in an attempt to achieve enhanced performance [4-6]. Energetic materials (EMs) are substances that store chemical energy and are capable of liberating this chemical energy to perform various effects, such as detonation, deflagration, and burning, accompanied with both heat (thermal) and pressure effects [7]. EMs generally can be classified into various categories, *i.e.* explosives, propellants, and pyrotechnics [3].

Thermites are mixtures that create a high concentration of heat energy, which usually comes in the form of molten reaction products. Thermite compositions contain a metal oxide as the oxidizer, and a metal (usually aluminum) as the fuel, although other active metals can be used [8, 9]. Various different oxidizers have been investigated to date, such as Fe_2O_3, MoO_3, $KMnO_4$, CuO, NiO, MnO_2, WO_3, SnO_2, and SiO_2 [10, 11]. Table 1 lists the thermo-physical properties of different thermite reactions [9].

Table 1. Thermo-physical properties of various thermite reactions [9, 12]

Reactants		Adiabatic reaction temperature (without phase changes) [K]	Gas production		Heat of reaction	
Constituents	Density [g·cm⁻³]		Moles of gas/100 g	g of gas/g	[kJ·g⁻¹]	[kJ·cm⁻³]
$2Al + Cr_2O_3$	4.190	2789	0	0	2.6	10.9
$2Al + 3CuO$	5.109	5718	0.5400	0.3431	4.1	20.8
$2Al + 3Cu_2O$	5.280	4132	0.1221	0.0776	2.4	12.7
$2Al + Fe_2O_3$	4.175	4382	0.1404	0.0784	4.0	16.5
$8Al + 3Fe_3O_4$	4.264	4075	0.0549	0.0307	3.7	15.7
$4Al + 3MnO_2$	4.014	4829	0.8136	0.4470	4.8	19.5
$2Al + MoO_3$	3.808	5574	0.2425	0.2473	4.7	17.9
$4Al + 3SnO_2$	5.356	5019	0.2928	0.3476	2.9	15.4
$10Al + 3V_2O_5$	3.107	3953	0.0699	0.0356	4.6	14.2
$4Al + 3WO_2$	8.085	4176	0.0662	0.0675	2.1	16.9
$2Al + WO_3$	5.458	5544	0.1434	0.1463	2.9	15.9

Recent developments in the area of metallic fuels have largely focused on ultra-fine powders [13, 14]. The reduction in thermite fuel and oxidizer particle sizes, ranging from micrometer to nanometer scale dimensions, considerably increases the surface area to volume ratio, allowing more fuel to be in direct contact with its oxidizer. Nanoscale particles permit greater intermixing and reduce the diffusion distance between fuel and oxidizer particles. As a result, the reaction progresses with a maximum rate and offers high energy release rates and high pressures [15-17], as shown in Figure 1.
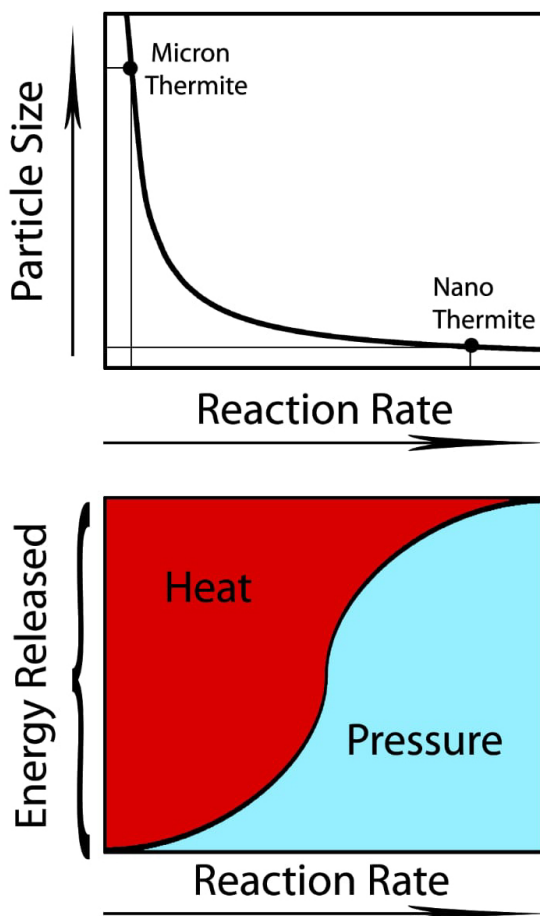

Figure 1. Effect of reactant particle size on the reaction rate and the energy released [16]

2 Nano-thermites, Superthermites (MICs)

The term nano-thermite refers to the particle sizes used for these energetic mixtures, in contrast to the more familiar thermite types of reaction in which the particle sizes are in the order of microns [18]. The term metastable intermolecular composites (MICs) comes from the fact that these mixtures of the metal oxide and aluminum are stable up to their ignition temperatures. On the other hand, the nano-thermite term comes from the fact that these thermites are composed of nano-sized materials that exhibit higher combustion characteristics when compared to their micron-sized relatives [19].

A distinctive characteristic of MICs, compared with high-explosives, is their high thermal diffusivity which leads to stronger heat propagation [11]. Figure 2 represents the heat of reaction *vs.* thermal diffusivity for different nano-thermites and conventional high explosives.
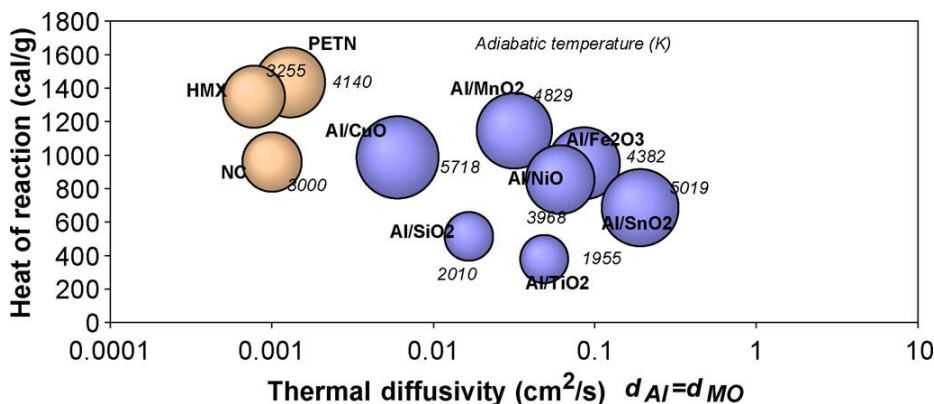
Figure 2.   Heat of reaction *vs.* thermal diffusivity for various types of energetic materials [10, 11]

Main reaction characteristics of nano-thermites depend on the particle size, shape, morphology, and the microstructure of its fuel and oxidizer components. A variety of MICs has been prepared in the forms of nano-spheres [20], nano-wires [21], nano-fibers [22], and nano-rods [23]. The particle sizes and bulk densities of these oxidizers and the degrees of their intermixing and interfacial contacting with the fuel (Alex) are frequently among the important factors that influence the ignition mechanism [21, 24].

The ignition mechanism is primarily influenced by the physical and chemical stability of the starting reactants and can be initiated by a variety of methods, including ignition by electrical power, laser radiation, impact or a combustion

wave from a chemical reaction [25]. The progress of nano-engineering technology has endeavoured to combine or synthesize inorganic energetic nano-composite materials, composed of metal oxide and fuel, to produce nano-thermites [26]. Nano-thermite fuels are electron-donors that react with the oxygen liberated from the oxidizer to produce an oxidized product with extraordinary heat [27]. Aluminium is the most common metallic fuel in use for thermite systems. At present, Alex (nano-Al) is the most widely used metallic doping particle due to its availability, simple production, low melting temperature and low cost, compared with other metallic fuels [8, 10, 11].

Research on novel nano-thermites requires wide ranging characterization techniques in order to fully recognize their behaviour, and for predicting suitable applications. Standard physical and chemical characterization is necessary to relate the chemical and physical properties of the prepared nano-thermite materials [20]. The basic characterization methods include:

– Transmission Electron Microscopy (TEM),
– Scanning Electron Microscopy (SEM),
– X-Ray Diffraction (XRD),
– Fourier Transform Infrared (FTIR) Spectroscopy,
– Particle surface area measurement (BET),
– Differential Scanning Calorimetry (DSC),
– Thermogravimetric Analysis (TGA),
– Closed-Bomb Calorimetry.

SEM and TEM, and its accompanying analytical techniques such as Energy Dispersive Spectroscopy (EDS), provide information about the nano-scale morphology and chemical elements present in a sample. XRD can provide information on the crystal structure and FTIR allows certain types of chemical bonds to be identified. DSC and TGA provide information on reaction temperatures, heat flow, and mass flow during an energetic reaction. This provides an understanding of the stages of the reactions as they relate to the phase changes of the different ingredients. These provide a comprehensive understanding of the chemical and physical properties of a sample [11, 28]. In addition, the sensitivities to different stimuli, such as electrostatic discharge, impact and friction, have a great influence on the application of nano-thermites. Increased sensitivity is usually accompanied by an increased reactivity of the material, which affects the combustion velocity of the high energy material [29].

3 Synthetic Methodology of Nano-thermites (MICs)

3.1 Physical mixing of individual nano-powders

One of the most common types of mixing for nano-powders is the mechanical mixing of individual nano-powder components (fuel and oxidizer) using ultrasonic waves or powerful mixers, to mix and combine nano-Al (Alex) and oxidizer particles in a liquid (*e.g.* acetone, hexane) to avoid agglomeration, then evaporation of the liquid and passing through different fine mesh trays to ensure breaking of any agglomerates [24, 30]. Al/MoO_3 MIC may be produced with 20-50 nm diameter and with 16 kJ·cm^{-3} total energy density and a high burning rate that reaches 1000 times that of macroscale thermites.

Figure 3 illustrates SEM micrographs of the Al/MoO_3 mixed together using hexane as the liquid blending medium [31]. Even though physical mixing of nano-powders (fuel and oxidizer) represents an inexpensive and uncomplicated method with the possibility for the production of large quantities, it has some drawbacks, such as the difficulty in mixing of ultrafine powders, the homogeneity of the final mixture (fuel, oxidizer) produced and the hazard as well as the danger of mixing of some sensitive fuels and oxidizers [9, 26].
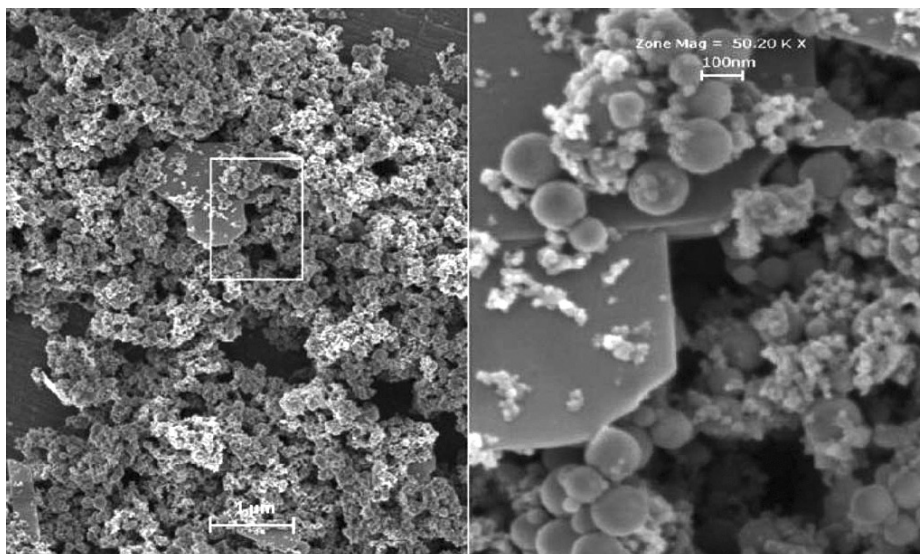
Figure 3.   SEM images of Alex particles mixed with MoO_3 particles [31]

3.2 Sol-gel process

In the sol-gel process technique, the nano-thermite is obtained by depositing aluminum nano-particles into the pores of an oxidizer [9] matrix. This method facitates the formation of a homogeneous dispersion of Alex within a nano-scale oxidizer framework matrix through reactions, in the solution phase, to disperse nano-particles in a liquid phase called a "sol" (colloidal solution) [32]. Through condensation, the sol gives a 3D solid network, called a "gel," with the open pores being occupied by the solvent [33]. The removal of the solvent by evaporation causes the collapse of the gel structure and leads to a xero-gel. While the supercritical drying method allows solvent removal without the collapse of the gel structure, this leads to a highly porous and low density material called an aerogel, characterized by uniform nano-scale particles and pores [33]. This process is efficient in generating highly intimate mixing between nano-thermite particles (fuel and oxidizer), but on the other hand, it has some limitations, which include a high level of porosity and scaling up difficulties [32]. A Al/Fe_2O_3 nano-thermite characterized by high surface area (300-400 $m^2 \cdot g^{-1}$) was developed by Tilloston [34] using the sol-gel technique, as shown in Figure 4.
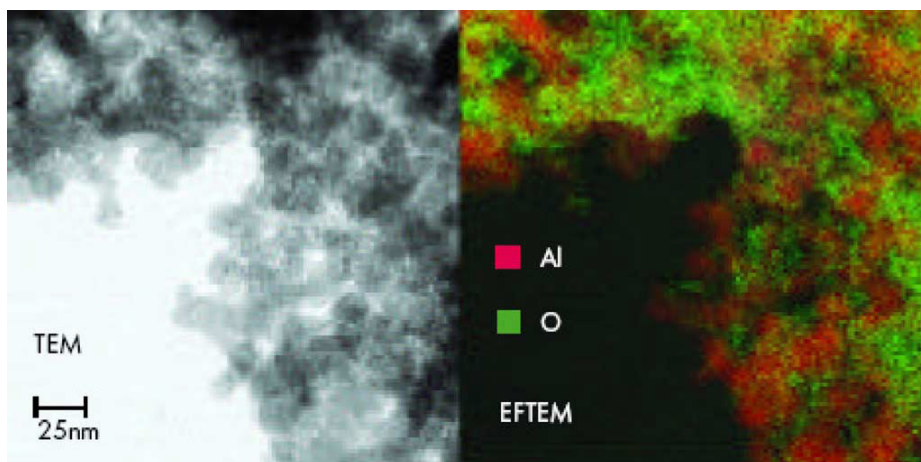
**Figure 4.** MIC based on (Al/Fe_2O_3) synthesized by the sol-gel process [35]

The sol-gel synthetic technique offers many advantages, such as compatibility with different energetic materials, safety, low cost, high porosity and high surface area. On the other hand, random distribution of the particles can cause a local disconnection between the fuel and oxidizer, and the existence of organic solvent impurities can reduce the reaction efficiency. In addition to the sol-gel

chemistry, the aero-sol-gel technology has also been employed to synthesize some nano-oxidizers, *e.g.* to prepare the analogous MICs with nano-Al metallic fuel as illustrated in Figure 5 [32].
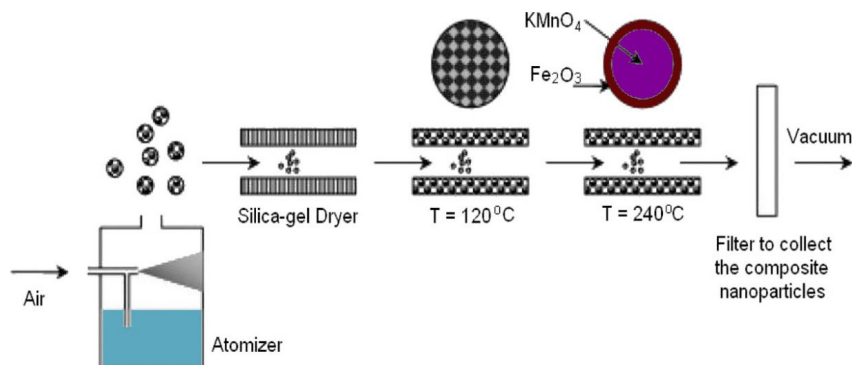
Figure 5.   Aerosol system for the synthesis of a core-shell nano-composite oxidizer [36]

A novel aerogel-based process was developed and reported by Prakash [11] to create nano-oxidizers ($KMnO_4$, Fe_2O_3) by coating a core of a strong oxidizer ($KMnO_4$) with a shell of relatively mild oxidizer (Fe_2O_3), as shown in Figure 6. The aero-sol-gel process used by Prakash is unconventional technology developed by intense investigation of the effect of nano-oxide thickness on the reaction rate. However, it has yet to be scaled up [36].
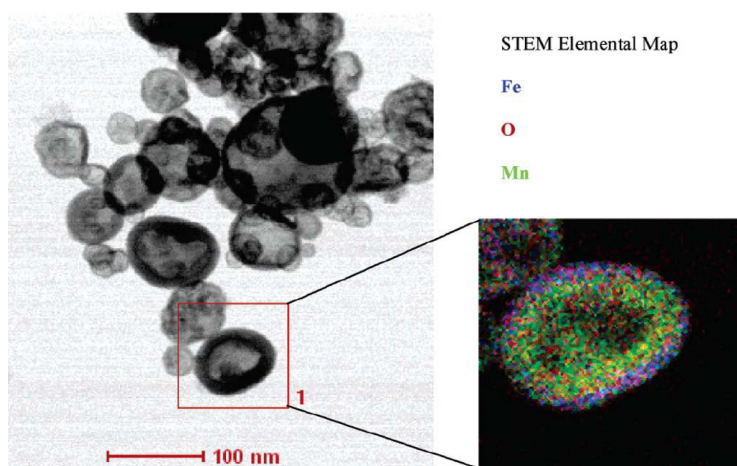
Figure 6.   TEM graph and STEM elemental map of nano-$KMnO_4$ coated with Fe_2O_3 [35]

In this method, an aqueous solution of $Fe(NO_3)\cdot39H_2O$ and $KMnO_4$ is sprayed as droplets (1 μm in diameter). The environment is dried. The aerosol is then thermally cured. Initially, it is maintained above the decomposition temperature of iron nitrate (typically 120 ºC), and then the temperature is increased to about 240 ºC. The 0.6 μm composite particles are then collected on a filter. At 120 ºC, iron nitrate decomposes into Fe_2O_3, intimately covering the solid permanganate. At 240 ºC, the permanganate melts, and the Fe_2O_3 aggregates around the $KMnO_4$ particles.

Reactivity experiments were performed and the reactivity was found to be adjustable over a relatively large range by varying the thickness of the iron oxide. The technique results in intimate contact between the reactants, the oxide coating thickness on each nano-particle is nano-scale and can be precisely controlled to lower the ignition temperature without reaction inhibition.

These MICs, characterized by higher surface areas (100-1000 $m^2\cdot g^{-1}$), afford better combustion performance due to the higher porosity and high surface area with porosity, that allows more intimate mixing between fuel and oxidizer particles with noticeable enhancement in heat transfer.

3.3 Vapour deposition (VD)

Vapour deposition (VD) is a chemical process used for the deposition of thin (layers) films of different materials, where the substrate is subjected to volatile precursors, which react or decompose on the substrate surface to produce the deposited layer, with thicknesses in the range of 20 nm to 2 μm [37]. VD was developed originally for joining applications [38]. It is often used in the semiconductor industry for the deposition of thin films of various materials [11].

Tappan *et al.* [37] employed the VD technique to deposit a thin film of the high explosive, pentaerythritol tetranitrate (NP), while Vine *et al.* [40] succeeded in the use of VD for Ti/Al and Ti/C, with a remarkable enhancement in the burning rate of the multilayer nano-composite. Blobaum *et al.* [39] reported a simple deposition process for Al/CuO_x multilayer nano-foils deposited onto silicon substrates in an inert medium (argon), as shown in Figure 7. The vapour deposition method for the creation of MICs has an obvious advantage, the diffusion distances between fuel and oxidizer in the product are reduced by up to 10-1000 times when compared to MICs created by physical mixing of powders, with a minimum presence of impurities, and thus a noticeable enhancement in reactivity can be achieved.
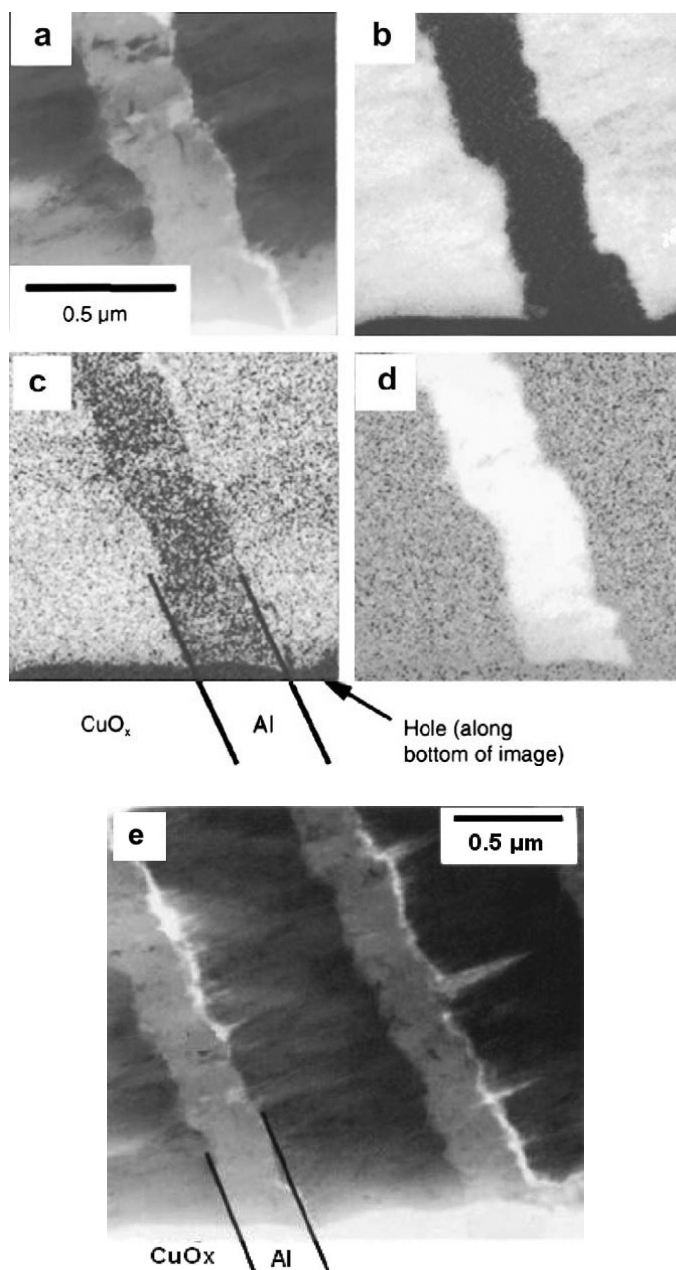
Figure 7.   TEM image of Al/CuO$_x$ multilayer nano-foils (a) Bright field image.
(b) Cu map (L2,3 edge, 931 eV) (c) O map (K edge, 535 eV).
(d) Al map (K edge, 1560 eV) [39, 40]

3.4 Arrested reactive milling (ARM)

ARM (high energy ball milling) has been applied by Ward *et al.* [41] to produce energetic composites of aluminum with other metal oxides such as Fe_2O_3 and MoO_3 in the micron-size range. Swati *et al.* [42] published work on the application of ARM to the preparation of reactive nano-composites based on Al-MoO_3, using selected milling conditions to initiate the reaction, varying the milling medium and the quantity of the process control agent used. Tawfik *et al.* has also described the preparation of nano-composites and their influence on the burning rate of composite solid rocket propellants (CSRP) [43], and the influence of energetic nano-composites prepared by high energy ball milling on thermal behaviour, safety and heat of combustion for CSRP [44].

ARM depends on the discontinuous process of exothermic reactions during the high energy ball milling process, which might result in mechanical initiation of the composite materials [42]. The main disadvantage of this process is the risk taken during the preparative method.

3.5 Nano-structuring synthesis methodology

3.5.1 Atomic layer deposition (ALD)

ALD is an ideal technique for depositing ultrathin films with high conformity and precise thickness control. The ALD method provides a unique opportunity to deposit uniform and conformal oxidizer coatings on fuel particles in order to fabricate an ''all-in-one'' enhanced nano-thermite reaction [45]. For instance it utilizes continuous gas pulses to deposit a unique thin layer. ALD has been used to deposit various metal oxides, such as NiO, Co_3O_4, and WO_3, on any selected substrate (fuel), for example on Al metallic fuel, to form an MIC [46].

3.5.2 Nano-porous silicon with oxidizer

Porous silicon (PSi) is a form of chemically treated elemental silicon that contains nano-pores in its microstructure, and offers a large surface area to volume ratio, in the range of 500 $m^2 \cdot cm^{-3}$, as illustrated in Figure 8.
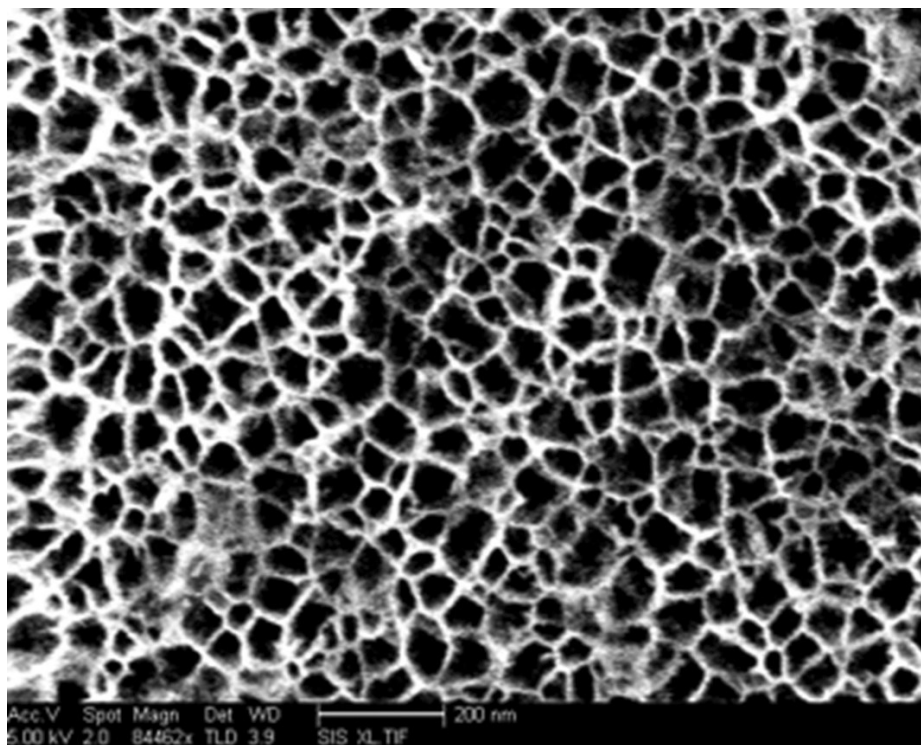
Figure 8.   Porous silicon (PSi) [47]

Electrochemical etching of silicon in solution using HF and H_2O_2 is an efficient method for obtaining Psi [49]. The degree of porosity and pore size can be tailored by controlling the acid concentration and the initial silicon. Silicon nano-pores can be filled with various oxidizers *e.g.* ($Ca(ClO_4)_2$, $KClO_4$, $NaClO_4$, sulfur, *etc.*) [12]. These results favoured PSi-based nEMs for industrial applications, as a component of airbag initiators.

Laucht *et al.* [48] measured various MICs based on PSi (PSi/$Ca(ClO_4)_2$ and PSi/$Na(ClO_4)_2$) in a calorimetric bomb and noted enhancements of the heat of reaction of 8.6 and 9.2 kJ/g, respectively. Consequently, MICs based on PSi can be incorporated into highly energetic systems [12, 48].

3.5.3 Nano-wires
This process is based on forming nano-porous alumina templates by initial electrochemical anodization of Al foil, followed by electrochemical deposition of Fe nano-wire inside the alumina nanopores. Finally, annealing of the Fe nano-

wires into Fe_2O_3 nano-wires with complete removal of the remaining alumina walls is performed with accurate control of the oxidizer and fuel dimensions at the nano-scale [49, 50], as illustrated in Figure 9(a).

Menon *et al.* [50, 51] reported the fabrication of an MIC based on Al/Fe_2O_3 by embedding Fe_2O_3 nano-wires (50 nm diameter of a single nano-wire) inside a thin Al film, with a density of about 10^{10} wires·cm^{-2}. An SEM micrograph of a high-density Fe_2O_3 nano-wire embedded in an Al film is illustrated in Figure 9(b).
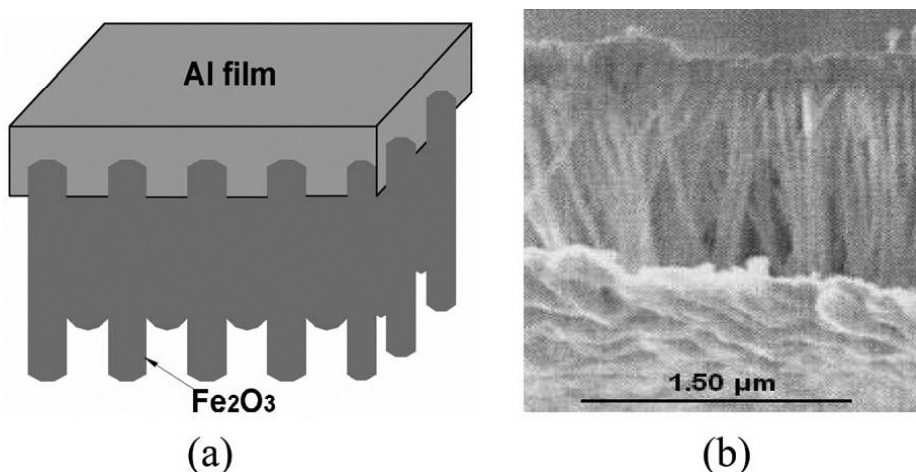

Figure 9.   Al/Fe_2O_3 MIC: (a) schematic, and (b) SEM image [50, 51]

Different studies showed that the use of CuO nano-wires resulted in improved mixing between the fuel and oxidizer components of the MIC, and consequently facilitated a low-temperature ignition [21]. These measurements demonstrated that the pressurization rate from a composite of Al nano-particles and porous CuO nano-wires was about ten times that from an Al nano-particle and CuO nano-particle MIC. Other means, such as the fabrication of the core-shell nanostructures [52] and intermetallic multilayers [53], were recently developed to enhance the energetic properties of MICs. The core/shell nano-wire based thermites indeed exhibited an improved mixing homogeneity and low activation energy [25]. The main advantage of this approach is the precise control of oxidizer and fuel dimensions at the nano-scale. The nano-wire technique avoids the presence of impurities and Al oxidation at the fuel-oxidizer interface before ignition.

3.5.4 Self assembly

One interesting technique is the self-arrangement of fuel nano-particles around the oxidizer, where the fuels or the oxidizers arrange themselves in an inorganic solution or by applying specific polymers. Kim and Zachariah [54] presented a method to synthesize MICs, in which the Al and Fe_2O_3 self-assembly is controlled by the electrostatic forces that exist between charged aerosol particles. The nano-Al particles then entirely surround the surface of the Fe_2O_3 particles with intimate contact. The authors compared the reactivity of the resulting Al/Fe_2O_3 with a randomly assembled Al/Fe_2O_3. The measured heat of reaction was found to be 1.8 *versus* 0.7 kJ/g for the randomly assembled material [54].

A polymer chain was employed to bind the main nano-thermite constituents (CuO and Al), as illustrated in Figure 10. The resulting polymer self-assembled Al/CuO MIC is shown in Figure 11. The measured burning rate reported by the authors was 2000 m/s, which is comparable to some EMs [11, 55].
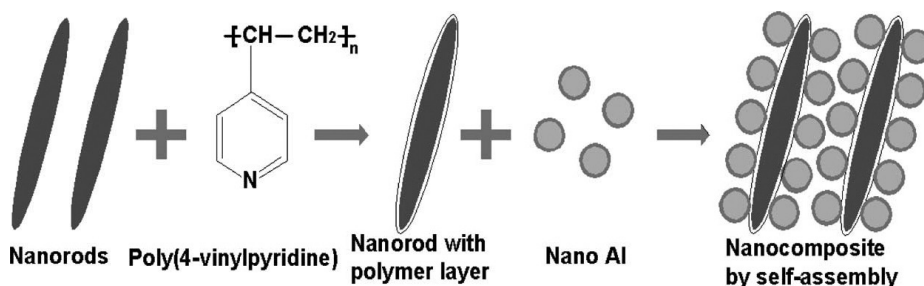
**Figure 10.** Schematic of nano-Al self-assembly around CuO nano-rods
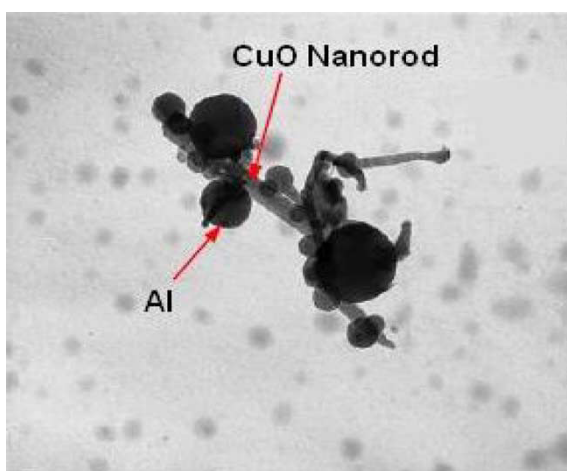
**Figure 11.** TEM image of nano-Al assembled around CuO nanorods

3.6 Novel nano-thermites based on carbon nano-materials

Carbon nano-materials (CNMs), such as carbon nano-tubes (CNTs) and carbon nano-fibers (CNFs), are characterized by their high catalyzing ability and large surface areas, up to $700\,m^2{\cdot}g^{-1}$ due to their exceptional pore-rich structures [56, 57]. Developments in the field of carbon nano-materials (CNMs) has been widely used in EMs as carriers of energetic components by coating or encapsulation, thus forming safer advanced nano-structures with better performance [58, 59].

Elbasuney *et al.* [16, 17] described a method for synthesizing MICs based on CNMs, which affords uniform metallization for a distributed copper oxide layer through an annealing process at 250 °C, as illustrated in Figure 12. XRD diffractograms revealed highly crystalline CuO particles superimposed on the surface of the CNMs. The CuO coating can act as an effective oxidizer for aluminium particles in super-thermite applications. CNFs and CNTs were effectively coated with CuO particles along the fibers and tubes as indicated in Figures 13(c) and 13(d).
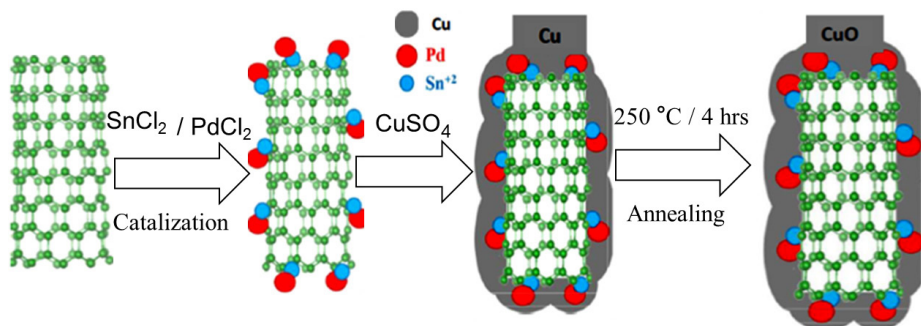
Figure 12. Schematic diagram for the preparation of CuO-coated CNMs [17]
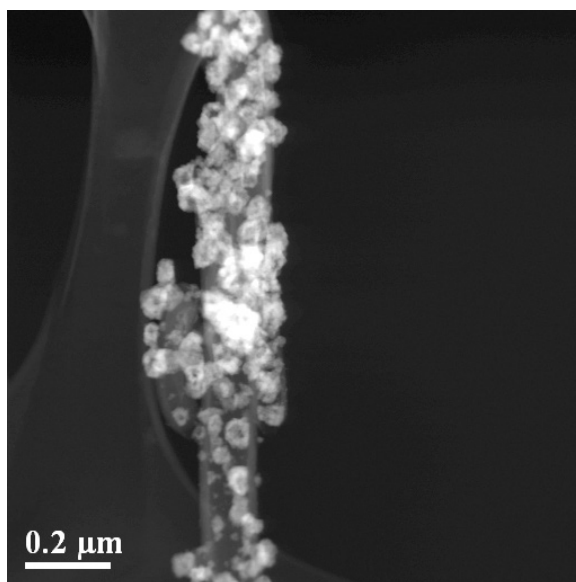
(a)
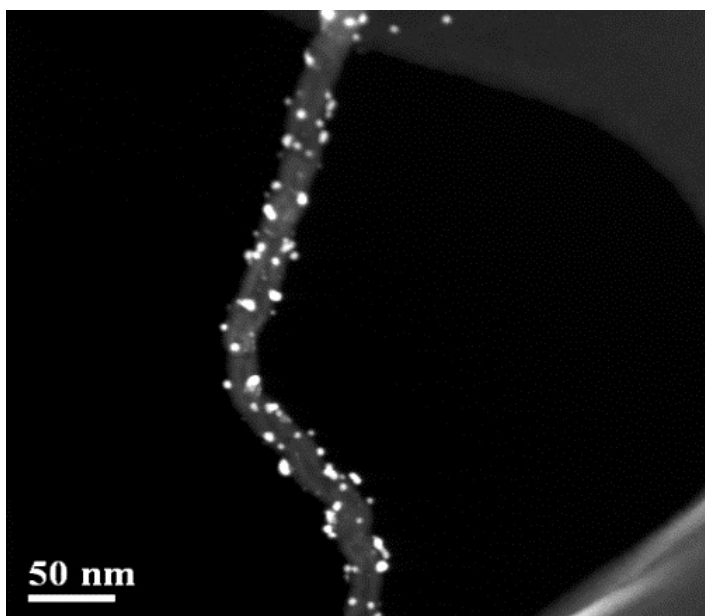
(b)

Figure 13. TEM micrographs of CuO-coated: (a) CNFs and (b) CNTs

This novel synthetic technique for hybrid thermite particles based on CNMs could promote interfacial contact between fuel and oxidizer particles to facilitate reaction at maximum rate. According to Shen [60], the presence of CNMs, nano-Al and (oxidizer) nano-CuO particles, tunes and enhances the MIC's reaction characteristics. The effective dispersion and stabilization of MICs into explosives could have a great impact on their performance [15-17].
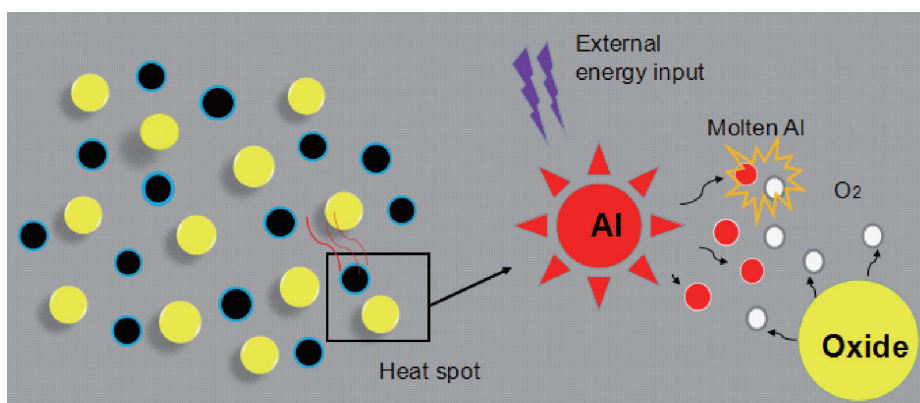
4   Thermite Mechanism of Action in Explosive Compositions

The incorporation of thermites in explosive compositions is reported by Jones *et al.* [61] who concluded that these compositions are characterized by good positive afterburning and extended fire balling, with the thermite optimum range being 8-10 wt.%. They assumed that when the high explosive is detonated, the action of the explosive itself creates a hot plasma in which the redox reaction of the reducing metal and the metal oxide is rapidly initiated. This plasma can aid or enhance the redox reaction by providing free electrons that facilitate the redox reaction, as illustrated in Figure 14. Thus, the resulting release of heat in the redox reaction can occur at a speed comparable to the detonation reaction [9, 61].

Figure 14. Schematic of the proposed thermite mechanism of action in explosive compositions

5   Applications of Nano-thermites Based on CNMs in Energetic Matrix Formulations

Elbasuney *et al.* [15-17] presented a superficial novel method for incorporating MICs based on CNMs and colloidal binary nano-thermite mixtures into an energetic matrix (molten TNT), where the developed nano-thermite particles were stabilized in an organic liquid and effectively integrated into the energetic matrix (TNT). This effective integration of colloidal Al/CuO binary nano-thermite mixture offered enhanced shock wave strength by 30% relative to an Al/TNT nano-composite, along with an increase in the total heat released by Alex/TNT, by 31% according to DSC measurements. The authors attributed this enhancement to the fact that these super thermite reactions were developed in the colloidal state and effectively integrated into the TNT.

MICs based on CNMs, increased the shock wave strength by 6.5% for CuO-coated Al/CNFs binary mixtures, and by 15.5% for CuO-coated Al/CNTs binary mixture. The superb performance of CuO-coated CNTs was ascribed to the extensive interfacial surface area of CNTs, allowing it to act as an ideal carrier for highly energetic particles. According to Elbasuney *et al.* [16], this new synthetic trend could open the route for the manufacture of different appropriate MICs for the effective development of advanced nano-composite cast metalized formulations. The mixtures of a nano-thermite with high explosives may offer interesting practical triggering potential, and present more promising developments. In addition, the thermal behaviour of nitrocellulose-based thermites was studied with the addition of different morphologies of Fe_2O_3 [62]. These results indicated that the catalytic performances of the super-thermites are highly relevant to the corresponding specific surface areas.

6   Conclusions

♦   Development of MICs is a very active and promising field that could lead to interesting achievements in the field of EMs. The enhancement of the performances of MICs and their application to EMs have been investigated and reported in this review.

♦   MICs offer high power and a high rate of reaction due to the high reduction-oxidation capability and high thermal diffusivity. Several techniques can be used and tailored to synthesize super-thermites with a wide range of chemical and energetic properties.

♦   Powder mixing, sol-gel, synthesis of MICs based on nano-PSi, sputtering,

and multilayer nano-foils, are efficient and promising techniques for MIC synthesis, particle size control and precise layer thickness control.

♦ A new trend to incorporate MICs based on CNMs and colloidal binary nano-thermite mixtures into an energetic matrix (TNT) was effectively done using a liquid blending technique.

♦ Even though formulating MICs with enhanced rates of energy-release, but precise control of the reactivity of nEMs, needs further research. However, except for TNT, the application of MICs in high explosive formulations for a combined effect of the formulations requires further research.

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