



Full Length Article

Stabilized super-thermite colloids: A new generation of advanced highly energetic materials



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ARTICLE INFO

Article history:

Received 19 February 2017

Received in revised form 4 May 2017

Accepted 5 May 2017

Available online 8 May 2017

Keywords:

Hydrothermal synthesis

Nanoparticles

Nanocomposites

Steric stabilization

Colloids

Super-thermites

Energetic materials

ABSTRACT

One of the great impetus of nanotechnology on energetic materials is the achievement of nanothermites (metal-oxide/metal) which are characterized by massive heat output. Yet, full exploitation of super-thermites in highly energetic systems has not been achieved. This manuscript reports on the sustainable fabrication of colloidal Fe₂O₃ and CuO nanoparticles for thermite applications. TEM micrographs demonstrated mono-dispersed Fe₂O₃ and CuO with an average particle size of 3 and 15 nm respectively. XRD diffractograms demonstrated highly crystalline materials. SEM micrographs demonstrated a great tendency of the developed oxides to aggregate over drying process. The effective integration and dispersion of mono-dispersed colloidal thermite particles into energetic systems are vital for enhanced performance. Aluminum is of interest as highly energetic metal fuel. In this paper, synthesized Fe₂O₃ and CuO nanoparticles were re-dispersed in isopropyl alcohol (IPA) with aluminum nanoparticles using ultrasonic probe homogenizer. The colloidal thermite particles can be integrated into highly energetic system for subsequent nanocomposite development. Thanks to stabilization of colloidal CuO nanoparticles in IPA which could offer intimate mixing between oxidizer and metal fuel. The stabilization mechanism of CuO in IPA was correlated to steric stabilization with solvent molecules. This approach eliminated nanoparticle drying and the re-dispersion of dry aggregates into energetic materials. This manuscript shed the light on the real development of colloidal thermite mixtures and their integration into highly energetic systems.

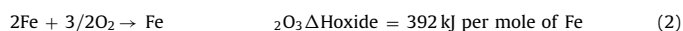
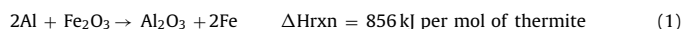
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1. Introduction

For ordinary organic explosives, it is well known that the available heat of explosion is limited to the heats of combustion of ordinary fuel elements (C, H) [1–3]. A simple way to increase the overall released energy, can be achieved by integrating elemental fuel into the explosive substance [3–5]. Aluminum fuel can react with free oxygen available in the explosive plasma formed upon detonation to produce aluminum oxide and significant additional heat [6,7]. However, most conventional explosives produce little free oxygen in the explosion plasma. If an oxidizer is present (as in the case of thermite) the oxygen would be more readily available for oxidation to take place (Fig. 1) [8–10].

Thermites (metal oxides/metal) are extremely exothermic reactions which can offer high energy density up to 16736 J/g compared

with 2094 J/g for TNT [1,12]. The rate of thermite reactions is limited by the diffusion of the particles and is comparatively low; the fuels undergo combustion at the point of contact with oxidizer [12–14]. Meta-stable intermolecular composites (MICs) are a subclass of thermites [15–17]. While comprised of the same materials as conventional thermites, MICs have particle sizes or inter-particle distances in the nanometer range [18,19]. This drastic reduction in particle size reduces the heat and mass diffusion distance between the fuel and oxidizer particles, thus permitting decreased ignition times and increased reaction rates [20–22]. Thermite reactions are extremely exothermic and run with self-sustaining oxygen content [11,23,24]. It should be noted that the metal formed in the redox reaction could potentially undergo combustion in the presence of excess oxygen and high temperature, for example:



Since one mole of Al-Fe₂O₃ thermite reaction produces two moles of iron, the produced metal fuel can be further oxidized by air oxygen. The total maximum energy that could be produced is

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Table 1
Thermophysical properties of thermite reactions.

Reactants		Adiabatic reaction temperature (K)	Gas production		Heat of reaction	
Constituents	Density		Without phase changes	Moles of Gas/100g	g of gas/g	KJ g ⁻¹
2Al+Cr ₂ O 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 ₂ O	5.280	4132	0.1221	0.0776	2.4	12.7
2Al+Fe ₂ O ₃	4.175	4382	0.1404	0.0784	4.0	16.5
8Al+3Fe ₃ O 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



Fig. 1. High speed video image of the first moment of nanothermite foam combustion [11].

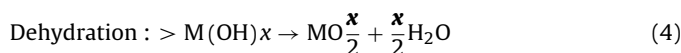
1640 kJ/mol; this can be converted to an energy density of 7.66 kJ/g [5]. Thermite reactions can find wide applications in highly energetic systems due to the high attainable heat and temperature. Table 1 tabulates the thermophysical properties of thermite reactions [5].

Yet, full exploitation of super-thermites in highly energetic systems has not been achieved. It has been reported that formulations based on super-thermites can offer a thermobaric effect and after-burning action with extended fire balling. The preferable range of thermite in highly energetic systems was reported to be 10–12 wt% [5]. Fe₂O₃ and CuO are ones of the most common oxidizers for thermite applications in terms of performance, cost, and availability. The sustainable fabrication of such oxides at the nanoscale is vital for super-thermite applications [16,21,24]. There have been many classical techniques for MICs synthesis including mechanical stirring [23], arrested reactive milling [1], and sol-gel technology [14]. However mechanical mixing requires the use of nanoscale starting materials [25]; arrested reactive milling cannot offer mono-dispersed particles as well as there is a great chance for complete oxidation of reactive metal during processing [1], sol-gel techniques require drying and sintering which will induce extensive aggregation with significant decrease in surface area and reactivity [14,26]. There is a great advantages for any approach that can offer sustainable fabrication of mono-dispersed particles that can be successfully isolated, and used in subsequent nanocomposite manufacture; such technique is hydrothermal synthesis [27].

Recently, hydrothermal synthesis is becoming one of the most valuable nanomaterial fabrication technologies and it has an edge over all other processing techniques [26–33]. It is an ideal technique for very fine powder processing with high purity, narrow particle size distribution, and controlled stoichiometry [34]. Through hydrothermal synthesis, the nanoparticle surface properties can be significantly changed from hydrophilic to hydrophobic and vice versa by the proper selection of the surface coating agent [33,35].

1.1. Hydrothermal synthesis of nano-oxides

The employed fluids for hydrothermal synthesis are subcritical or super-critical fluids. The enhanced levels of OH⁻ at the critical point can be exploited for nanoparticle synthesis [36,37]. Under these conditions hydrolysis of metal salt (Eq. (3)) is immediately followed by a dehydration step (Eq. (4)).



Super-critical fluid is an ideal medium for nanoparticle synthesis; where massive nucleation could take place [34]. The formed particles will be carried outside the reactor without further growth. A schematic for continuous hydrothermal synthesis is demonstrated in Fig. 2. In this technique the super-critical water (ScW) flow (A) is instantly mixed with cold metal salt (B). Nanoparticles are formed at the interface of the two fluids inside the reactor (R) and the buoyancy of the heated flow caused the nanoparticle slurry to be carried outside the reactor. The nanoparticle flow stream is cooled down prior to collection at point (D).

It is established that mono-dispersed particles were formed as nucleation and subsequent particle growth are the same for all particles [34,38,39]. Evans reported on the hydrothermal synthesis of Fe₂O₃ particle with controlled size (ranging from 5 to 50 nm) by controlling the super-critical fluid temperature (Fig. 3) [40].

The particles made at higher temperatures were larger and more crystalline than at lower temperatures, and also had a much broader size distribution [40].

This study reports on the sustainable fabrication of mono-dispersed colloidal Fe₂O₃ and CuO for thermite applications. Colloidal CuO particles flocculated within 30 min. Synthesized Fe₂O₃ nanoparticles demonstrated stable colloid; this was correlated to electrostatic stabilization via electric double layer associated with each particle [41]. The formulated Fe₂O₃ nanoparticles were flocculated from their synthesis medium by distorting the electric double layer associated with each particle. Fe₂O₃ and CuO particles were harvested and re-dispersed in isopropyl alcohol (IPA) with aluminum nanoparticles for subsequent nanocomposite manufacture. CuO demonstrated sterically stabilized colloid in IPA. This could offer enhanced nanoparticle dispersion as IPA is the dispersing medium for super-thermite and a good solvent for energetic organic systems. CuO/Al is one of the most gaseous producing thermites, the formed Cu metal can be transformed into gas due to its low boiling point (1000 °C) [1]. During energetic material conversion, CuO/Al and Fe₂O₃/Al thermite reactions would proceed with maximum rate. This manuscript reported on novel approach for the real development of colloidal thermite mixtures and their subsequent integration into highly energetic systems. The developed super-thermite colloids can find wide applications into different highly energetic systems for instance pyrotechnic compositions, solid rocket propulsion systems, as well as advanced highly energetic materials with combined action (detonation and combustion).

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