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Tuning the morphological, ignition and combustion properties of micron-Al/CuO thermites through different synthesis approaches

Sili Deng[a,b,1], Yue Jiang[c,1], Sidi Huang[a], Xinjian Shi[a], Jiheng Zhao[a], Xiaolin Zheng[a,*]

[a] Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA
[b] Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[c] Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

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ABSTRACT

Aluminum (Al)-based thermite, due to its high energy density and low cost, has found wide applications in aerospace propulsion, explosion, pyrotechnics, thermal batteries, and power generations. Though significant efforts have been devoted to improving the ignition and combustion performance of Al-based thermites by using nano-Al, micron-Al (m-Al) remains of practical importance over nano-Al due to its lower cost and smaller dead mass. For m-Al based thermite, the main approach to improve its ignition and combustion performance is to bring Al and metal oxide as close as possible to facilitate the oxidizer diffusion process. Herein, we demonstrated two simple synthesis methods, *i.e.*, the precipitation (PC) method and displacement (DP) method, to prepare m-Al/CuO thermites with the intention to bring Al and CuO to shorter diffusion distance and achieve better dispersion. The PC-thermites have flocculent nanostructured CuO closely attached to the surface of m-Al, and the DP-thermites have a dense shell of CuO coated on the surface of m-Al. Both PC- and DP-thermites have reduced agglomeration and diffusion distance over the traditional mechanically mixed (MM)-thermites that have randomly distributed and agglomerated CuO and m-Al. Consequently, both PC- and DP-thermites exhibit shorter ignition delay time, lower reaction onset temperatures, higher heat release, larger pressure rise, and extended reactivity limits than MM-thermites. Particularly, PC-thermites, due to their flocculent structures, exhibit the shortest ignition delay time, lowest reaction onset temperature, and highest amount of heat release. Moreover, the superior ignition and combustion performance of PC- and DP-thermites is more pronounced under high heating rates over low heating rates. Similar PC and DP methods are applicable to prepare diverse thermites with reduced diffusion distance and improved dispersion to improve their ignition and combustion properties.

1. Introduction

Energetic materials composed of metal and metal oxide mixtures (*e.g.*, Al and CuO) are generally referred as thermites. Thermites have high energy density and large post-combustion temperature and pressure rise, so they are extensively utilized to provide heat and thrust in explosion, pyrotechnics, thermal batteries, and power generation [1–4]. Nevertheless, thermites are difficult to ignite and have slow energy release rates and incomplete reaction, hindering them from reaching their full potential in those applications. Those drawbacks of thermites come from two main reasons. Thermite reaction is a heterogeneous reaction that requires the diffusion of oxidizer in the condensed phase, which is inherently slow [5–7]. Furthermore, as the metal fuel is oxidized, the generated metal oxide accumulates on the surface of metal, inhibiting the further diffusion of the oxidizer into the metal [8,9].

To facilitate the diffusion process, a general approach is to reduce the diffusion distance by bringing metal fuel and metal oxide as close as possible and/or reducing the size of components to nanoscales [10]. Following these principles, much research effort has been devoted to the synthesis and characterization of nano-sized thermites (nanothermites). A recent review by Dreizin [11] summarized different synthesis methods for preparing nanothermites, including powder mixing [12–15], sol–gel [15,16], self-assembly [17–20], layered vapor deposition [21–24], and arrested reactive milling (ARM) [25,26]. In brief, the powder mixing method is also known as the mechanical mixing (MM) method, in which the component particles are physically mixed with or without liquid carrier. In the sol–gel processing, the fuel particles are imbedded in the pores of the oxidizer matrix to form a nanocomposite. For the self-assembly, surfactants are utilized to functionalize the

* Corresponding author.
E-mail address: xlzheng@stanford.edu (X. Zheng).
[1] Sili Deng and Yue Jiang contributed equally to this work.

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surface of component particles to achieve ordered arrangements. In the layered vapor deposition, component layers are coated on top of each other using vacuum deposition, forming layered nanofoils. In arrested reactive milling, the feedstocks are often micron-sized components and are refined to nanocomposites in a ball-milling reactor.

In spite of the high reactivity of nanothermites, the production of nano-Al (n-Al) is rather energy-intensive and costly [27]. n-Al has a significant portion of dead mass due to its relatively thick native oxide layer (2–6 nm) [28]. n-Al is of safety concern due to its sensitivity to electrostatic discharge, mechanical, and friction impact [29]. Moreover, n-Al particles are subject to agglomeration, resulting in reduced specific surface area [30–32]. Given these concerns of n-Al, thermites composed of micron-Al (m-Al) remain highly relevant to practical applications. There is a still great need to improve the ignition and combustion properties of m-Al based thermites, for which the typical approach is to coat m-Al with fluoride or to use energetic additives. For example, Sippel et al. mixed m-Al with fluorine-based additives to reduce Al agglomeration during combustion and promote gas generation and burning rate [33]. Ohkura et al. reduced the minimum flash ignition energy of m-Al by the addition of WO_3 nanoparticles, which have better light absorption [34]. Ilunga et al. [35] and Parimi et al. [36] sensitized m-Al/CuO thermite with more reactive energetic additives (Si/Bi_2O_3 thermites [35] and porous-$Si/NaClO_4$ [36], respectively).

Those pioneering work indeed demonstrated the potential to improve the ignition and combustion of m-Al, but there is a lack of systematic study to investigate how the synthesis method affects the morphology of m-Al thermites and how the morphology further influences their ignition and combustion properties. The importance of such a study was already demonstrated for n-Al thermites by Monk et al. [32], and this study demonstrated that the synthesis method of n-Al/CuO thermites (in the form of nanocomposites) significantly impact their combustion behaviors in different gas environments.

Herein, we investigate the effect of synthesis method on the morphology and ignition and combustion properties of m-Al based thermites. We choose Al/CuO as our model thermite system, as it is among the most investigated thermites due to their high energy density and reactivity [37–39]. For the synthesis, we focus on three synthesis methods that do not require any special equipment, *i.e.*, mechanical mixing (MM), the precipitation (PC) method and displacement (DP) method. We characterized the ignition and combustion performance of m-Al/CuO thermites prepared by these three methods by analyzing the trends observed in constant-volume vessel, bomb calorimetry, and differential scanning calorimetry tests. In general, PC- and DP-thermites have better dispersion and reduced diffusion distance of m-Al and CuO than MM-thermites, leading to shorter ignition delay and more efficient combustion. In particular, PC-thermites, with uniform dispersion and flocculent structures, exhibit the shortest ignition delay time, lowest reaction onset temperature, and highest amount of heat release.

2. Experimental methodology

Our objective is to study the effect of composition and morphology of m-Al/CuO thermites on their ignition and combustion properties. We will tune the morphology of m-Al/CuO thermites by using different synthesis methods. With the potential scalability in mind, we chose three simple synthesis methods to prepare m-Al/CuO thermites, *i.e.*, mechanical mixing, precipitation, and displacement methods, which are schematically illustrated in Fig. 1. These three methods do not require any special equipment but only beakers. The morphology and composition of the prepared thermite samples were characterized with scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and inductively coupled plasma mass spectrometry. Their ignition and combustion properties were quantified with constant-volume vessel, bomb calorimetry, and differential scanning calorimetry.

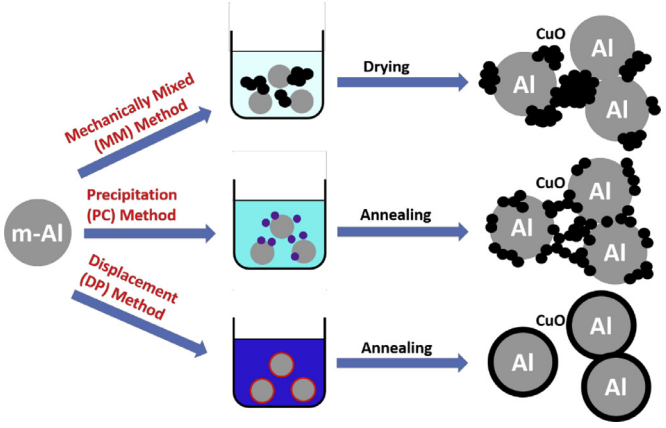

Fig. 1. The schematics of three different synthesis methods to prepare m-Al/CuO thermites and their expected morphologies.

2.1. Sample preparation methods for m-Al/CuO thermites

2.1.1. Mechanical mixing (MM) method

Mechanically mixed m-Al/CuO thermites were prepared as a control sample for comparison. For stoichiometric thermite mixtures ($2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$), 100 mg of m-Al particles (99.8%, 3.0–4.5 μm in diameter, Alfa Aesar, also used in other preparation methods) and 442 mg of CuO particles (< 50 nm in diameter, Sigma-Aldrich) were mixed in 15 ml of hexane and sonicated for 30 min. Then, the solvent hexane was vaporized at 80 °C for 1 h, and the particles were fully dried in a vacuum desiccator for 12 h.

2.1.2. Precipitation (PC) method

The PC method forms copper complex on top of m-Al particles. The copper complex is further converted to CuO by annealing. Since the copper complex might also precipitate in the solution, the final m-Al/CuO thermite will be a mixture of CuO and m-Al/CuO core/shell particles.

Specifically, to prepare stoichiometric Al/CuO thermite, first, 100 mg of m-Al particles were dispersed in 20 ml of anhydrous ethanol and sonicated for 10 min. Then, 4.5 ml of ammonium hydroxide solution (NH_4OH, 15%) was added into the suspension. After that, 12.9 ml of 100 g/l copper nitrate hemi(pentahydrate) ($Cu(NO_3)_2$-$2.5H_2O$, Sigma-Aldrich) ethanol solution was added into the suspension dropwise. After stirring for 3 h, the color of the suspension changed from gray to purple, indicating the formation of copper complex $Cu(NH_3)_4(OH)_2$ [40] in the solution and on the surface of m-Al. All the solid particles were collected by filtration and fully dried in a vacuum desiccator for 12 h. Finally, the dried particles were annealed on a hotplate at 250 °C for 20 min, and the color of the particles changed from purple to black, indicating the decomposition of $Cu(NH_3)_4(OH)_2$ to CuO [41].

2.1.3. Displacement (DP) method

The displacement method galvanically displaces Cu^{2+} by Al, forming Al/Cu core/shell particles. Then, Cu is further annealed to be CuO, forming m-Al/CuO core/shell particles.

Specifically, to prepare stoichiometric Al/CuO thermite, the $CuSO_4$-based stock solution was first prepared by dissolving 6 g of $CuSO_4$ (Sigma-Aldrich), 14 g of Ethylenediaminetetraacetic acid (EDTA, Sigma-Aldrich) and 28 g Triethanolamine (TEA, Sigma-Aldrich) in 1 l of de-ionized water. Then, NH_4OH aqueous solution

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