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Synthesis and ignition of energetic CuO/Al core/shell nanowires

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Abstract

Energetic thermites (mixtures of Al and metal oxides), due to their high energy densities, have broad applications in propulsion, thermal batteries, waste disposal, and power generation for micro systems. Reducing the sizes of Al and metal oxides down to the nanoscale has been shown to be effective in increasing their reaction rates and reducing their ignition delays. However, it remains a challenge to create mixtures of Al and metal oxides with nanoscale uniformity. Here we report synthesis and ignition studies on thermites with a new nanostructure, i.e., CuO/Al core/shell nanowires (NWs). The CuO NW cores were synthesized by the thermal annealing of copper films and served as templates for the deposition of Al shells by subsequent sputtering. The advantage of such a core/shell NW structure is that CuO and Al are uniformly mixed at the nanoscale. The onset temperatures of the exothermic reaction of the core/shell NWs were similar to those of nanoparticle (NP)-based thermites in terms of magnitude, insensitivity to equivalence ratios and sensitivity to heating rates. Moreover, the core/shell NW thermites, compared to NP-based thermites, exhibit greatly improved mixing uniformity and reduced activation energy for the thermite reaction.

Keywords: Nanoenergetic materials; Thermite; Nanowire; CuO/Al core/shell nanowire; Ignition

1. Introduction

Energetic thermites (mixtures of Al and metal oxides), due to their high energy densities and capacity for self-sustained reaction, are extremely energy efficient, and have broad practical applications ranging from propulsion, thermal batteries, material synthesis, waste disposal to power generation for micro systems [1–5]. However, one of the major limitations of thermites as energetic materials is their long ignition delay times [6]. Reducing the sizes of Al and metal oxide particles to the nanoscale has been demonstrated to be effective in facilitating the ignition process [7,8]. For example, Pantoya and Granier [9] have shown that the onset temperature of Al/MoO_3 composites was reduced by at least 300 °C when the Al particle size was decreased from several microns to below 100 nm. Pantoya and Granier [10] have also demonstrated that the ignition delay time of Al/MoO_3 composites using laser ignition was reduced from 1384 ms to around 20 ms by decreasing the average Al particle size from 10 μm to below 200 nm. Similarly, Brandstadt et al. [11] have shown that the onset temperature of the oxidation of Al in CO_2 decreased from around 920–940 °C to 500–510 °C while the Al particle size was reduced from 10 μm to 38 nm. In addition, nanoscale Al/MoO_3

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thermites were demonstrated to have burning rates ranging from 600–1000 m/s in an open-ended acrylic tube, which is 1000 times faster than the micron size thermites [12–14].

These nanoscale thermites (or nano-thermites) can be produced by many methods which were summarized in recent reviews [5,7,8,15], such as arrested reactive milling [6,16–19], powder mixing [13,20–22], self-assembly [23,24], and layered vapor deposition [25,26]. However, all of these methods suffer from certain shortcomings. For instance, although the mechanical mixing of Al with metal oxide nanoparticles (NPs), such as direct mixing in an ultrasonic bath using hexane or isopropanol [27], is simple, it cannot homogeneously mix Al and metal oxides with a large degree of spatial homogeneity due to aggregation of the same type of NPs. As such, these materials exhibit large scatter in their ignition and burning characteristics. Moreover, metal oxides synthesized or mixed in the solution phase typically contain hydroxyl groups, water, and hydrocarbons [23], that act as heat sinks by absorbing energy, and hence retard the ignition and flame propagation processes [28]. Blobaum et al. [25,29] demonstrated a different method to form highly uniform CuO_x/Al multilayer foils by alternatively depositing Al and copper oxide layers with well-defined thicknesses under high vacuum, but this fabrication process is costly, time-consuming and difficult to scale up. The above limitations have hindered the fundamental understanding and optimization of nano-thermites. Therefore, there is a critical need to develop new, simple and yet scalable methods to create well-defined thermites with nanoscale mixing and homogeneity for both fundamental studies and practical applications.

Recently, one-dimensional nanowires (NWs) have been used as templates to assemble nano-thermites for improved mixing uniformity. One approach is to coat metal oxide NWs with an adhesive polymer to bond Al NPs onto the sidewalls of NWs [23,24]. The advantage of this approach is that the cylindrical geometry of NWs allows a relatively larger number of Al NPs to be assembled to a single NW. Nevertheless, the attachment of Al NPs to the NWs is not uniform along the axial direction of NWs. Another approach is to directly deposit a layer of Al film with controlled thickness on top of metal oxide NWs to form uniform metal oxide/Al core/shell NW thermites [30,31]. However, studies on the second approach have been focused on the fabrication process for integration of the nano-thermites onto silicon wafers for potential applications in microelectronic mechanical systems. Fundamental ignition characteristics of these core/shell NW thermites were not systematically studied and no comparison with the conventional NP thermites was made.

In view of the above considerations, we have performed experimental determinations of the ignition and heat release characteristics of the CuO/Al core/shell NW thermites in helium environments by using differential scanning calorimetry (DSC). The CuO/Al core/shell NWs were synthesized by the thermal annealing of electroplated Cu film to grow CuO NWs, followed by Al film deposition by sputtering. The onset temperature of the exothermic reaction of the CuO/Al core/shell NWs was measured to be in the range of 550–570 °C, insensitive to the overall equivalence ratios, and to increase with increasing heating rates. The CuO/Al core/shell NW thermites have demonstrated two notable advantages over thermites consisting of CuO NPs and Al NPs: (1) significantly reduced activation energy for the thermite reaction, and (2) greatly improved mixing uniformity.

2. Experimental specifications

The fabrication process of the CuO/Al core/shell NWs is illustrated in Fig. 1. First, a layer of copper film was electroplated over a steel plate using a flash copper™ plating kit (Castwell Inc.) with a current density of 20 mA/cm^2, which yields a deposition rate of approximately 60 nm/min. We deposited a copper film of 1 μm thickness because it gives the optimal CuO NW density with a thin supporting CuO layer. Before electroplating, the steel plate was thoroughly cleaned with acetone, methanol, and isopropyl alcohol, in sequence, to remove any organic impurities and promote the adhesion of copper. Second, CuO NWs were grown by the simple thermal annealing method [32], in which the electroplated copper film was heated on a hotplate at 500 °C for 5 or 24 h under ambient conditions. After annealing, the color of the copper film changed from shiny brown to black (Fig. 1a, inset), indicating that Cu has been oxidized to CuO. Scanning electron microscopy (SEM, FEI XL30 Sirion, 5 kV) imaging (Fig. 1b) shows that CuO NWs have been formed with a perpendicular orientation with respect to the Cu film. Finally, a layer of Al film was deposited over the CuO NWs by magnetron sputtering under a vacuum level of 5×10^{-3} Torr. Magnetron sputtering was selected over other metal deposition techniques, such as electron beam and thermal evaporation, because it provides enhanced conformal coating, resulting in a uniform CuO/Al core/shell NW structure (Fig. 1c and d). Since the deposition rate on the sidewall of NWs is typically smaller than that on a flat surface, the actual thickness of the Al layer was always independently measured by SEM. The Al layer thicknesses analyzed in this paper were set to be 0.5, 1.0, 1.5 μm for a flat surface, and the actual shell thicknesses are around 100, 250, and 425 nm.

The morphology and surface coverage density of the CuO NWs can be easily tuned by varying the annealing temperature and time. For example,