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Generation of fast propagating combustion and shock waves with copper oxide/aluminum nanothermite composites

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Nanothermite composites containing metallic fuel and inorganic oxidizer are gaining importance due to their outstanding combustion characteristics. In this paper, the combustion behaviors of copper oxide/aluminum nanothermites are discussed. CuO nanorods were synthesized using the surfactant-templating method, then mixed or self-assembled with Al nanoparticles. This nanoscale mixing resulted in a large interfacial contact area between fuel and oxidizer. As a result, the reaction of the low density nanothermite composite leads to a fast propagating combustion, generating shock waves with Mach numbers up to 3. © *2007 American Institute of Physics*.

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Nanothermite materials are comprised of a physical mixture of inorganic fuel and oxidizer nanoparticles. Nonhomogenous distribution of fuel and oxidizer has been observed in the microstructures.[1] This produces random hot spot density distribution and decreases the propagation speed of the combustion wave front. It is, therefore, important to achieve homogenous mixing of the oxidizer and fuel components for faster reaction kinetics. This can be achieved by self-assembly of fuel around the solid oxidizer. Enhancement in the combustion wave speed has already been reported for composites containing porous oxidizers and fuel nanoparticles,[2,3] and also for electrostatically charged self-assembled composites.[4]

Recently, we reported that higher combustion wave speeds were achieved for the composites of ordered porous Fe_2O_3 oxidizer and Al nanoparticles[5] as compared with the one containing porous oxidizer with no ordering of the pores and Al nanoparticles. We have also reported the composite of CuO nanorods and Al nanoparticles exhibiting a combustion wave speed of 1500 ± 100 m/s, which enhances to 2200 m/s for the self-assembled composites.[6–8] Interestingly, these higher combustion wave speeds are comparable to the lower end values of the detonation velocities (e.g., 2000 m/s for hydrocarbon/alkylene-air mixtures,[9] 1500–2700 m/s for metallic azides and fulminates,[10] and about 3000 m/s for ammonium nitrate fuel oil) for explosives.[11]

In conventional explosives, the gases produced during the chemical reaction develop turbulence due to a combined effect of high pressure and rapid shearing of molecular layers generating a shock wave. In a process called deflagration-to-detonation transition (DDT), the wave propagates in the reactive medium creating localized high pressure at the hot spots and, after a certain run-up distance, rapid deflagration can transition to full detonation.[9] This distance depends on the dimensions of the shock tube and also the level of confinement.[9] In the case of low density superthermites, as the adiabatic reaction temperatures are several thousand degrees, the reaction products can volatilize rapidly[12] resulting in an increased level of turbulence and high localized pressures. Because of the low density and multiphase nature of reaction materials, the corresponding Chapman-Jouguet (CJ) pressure can be much lower than that of conventional solid explosives. However, it is not evident from the present work whether a DDT process is occurring in the case of nanothermites during self-propagation of accelerated combustion wave. Further work is needed to confirm it. The generated shock waves with pressures well below the CJ pressures of solid explosives have potential applications in many areas such as in geology, seismological techniques, biomedical applications,[13] bloodless scalpel,[14] and permeabilization of cells for drug and particle delivery.[15–17]

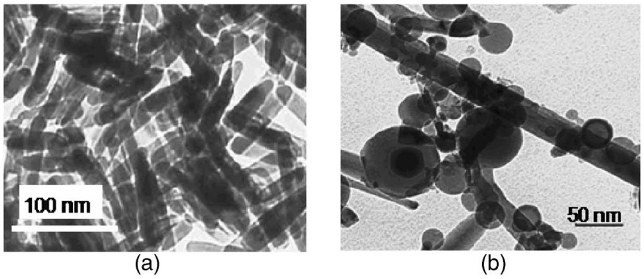

FIG. 1. TEM Images of (A) CuO nanorods and (B) self-assembled CuO nanorods/Al.

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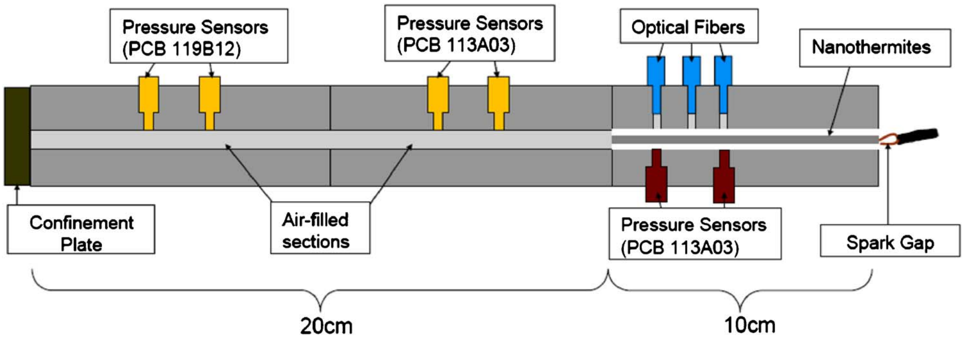

FIG. 2. (Color online) Schematic of the shock-tube setup used for the measurements. The pressure sensors in the nanothermite section of the tube (bottom) were only installed for density experiments.

The precursors $CuCl_2$, polyethylene glycol 400, and NaOH for CuO nanorod synthesis[18] were used without purification. Poly(4-vinylpyridine) was utilized for assembling CuO nanorods and Al nanoparticles with size of 80 nm. The optimum combustion wave speed was determined by performing a series of experiments varying the equivalence ratio Φ,[19] defined as

$$\Phi = \frac{(\text{fuel/oxidizer})_{\text{actual}}}{(\text{fuel/oxidizer})_{\text{stoichiometry}}}, \quad (1)$$

between 0.6 (fuel lean) and 1.8 (fuel rich). Details of these results are presented elsewhere.[8] For this paper, we have chosen a Φ value of 1.6 as it produced maximum combustion wave and shock wave speeds. The transmission electron microscopy (TEM) images of CuO nanorods and CuO nanorods assembled with Al nanoparticles are shown in Figs. 1(a) and 1(b), respectively.

Pressure wave measurements were carried out in a shock-tube system, as shown in Fig. 2. The tube was comprised of three segments, each 10 cm in length. One segment housed the nanothermite material, and the other two sections contained ambient atmosphere. The section containing nanothermites had fiber optics (Thorlabs M21L01) coupling the inside of the tube to photodiodes (Thorlabs DET210) for measuring the velocity of the combustion front. This section of the tube was separated from the other sections by an aluminum diaphragm (100 μm thick). The latter two segments each had pressure transducers (PCB models 113A03 and 119B12) mounted along them for measurements of the pressure wave velocity. All three segments were clamped together, and a confinement plate was placed over the end of the tube opposing the nanothermite material. The output of the photodiodes was recorded using a Tektronix oscilloscope TDS460A. The signal from the pressure transducers was measured using National Instruments (NI) data acquisition (DAQ) hardware, and LABVIEW control software.

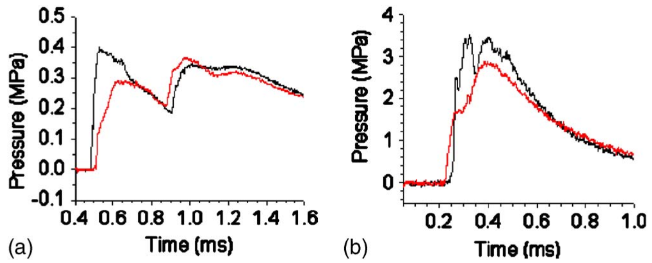

FIG. 3. (Color online) (A) Typical pressure-time history in the air-filled section of the tube. (B) Typical pressure-time trace in the nanothermite section.

For each experiment, a polycarbonate tube with 3.175 mm inner diameter was loaded with nanothermite material and inserted into the first segment. The energetic reaction was triggered by a spark generator, and the leading photodiode was used to trigger data acquisition on both the oscilloscope and NI DAQ. The combustion wave speed of the energetic material was determined based on the time of arrival of the flame at each optical fiber. Similarly, the pressure wave velocity was determined by the temporal response of the pressure transducers. The typical time history for the pressure sensors in the air-filled section is shown in Fig. 3(a). Incident and reflected wave fronts are recorded since the pressure wave reflects off the confinement plate at the end of the tube. The typical pressure-time trace in the nanoenergetic section of the tube is shown in Fig. 3(b).

In one set of experiments, two nanothermite compositions, the physically mixed and self-assembled samples, were compared. In another set of experiments, the percent theoretical maximum density (%TMD) of physically mixed CuO nanorods and Al nanoparticles was varied by loading different amounts of powder into the tube. The volume of the polycarbonate tubes used was 0.8 cm^3, and the TMD of the CuO/Al composites is 5.36 g/cm^3. As the mass of nanothermite material was varied from 100 to 700 mg, the %TMD changed from 2.4% to 16.5%. An additional pressure measurement was made directly on the tube containing the nanothermite. The sensors for this measurement are pictured directly below the optical fibers shown in Fig. 2. From Table I, we observe that the self-assembled composite produced a higher combustion rate and pressure wave velocity compared to the physically mixed material due to a higher interfacial contact area. In the other experiment, with an increase in density, the combustion wave velocity was found to decrease from ~1400 to ~700 m/s; however, the shock wave velocity increased from ~500 to ~850 m/s (Fig. 4). It was also observed that the pressure of the combustion zone increased with the increase in the density. At higher% TMD, the gas inside the air column compressed to a higher density resulting in a higher shock wave speed.

In an attempt to explain the observed self-propagating reaction and generation of shock waves for our nanothermites, we may consider the simplest model, CJ theory. For

TABLE I. Shock wave velocities of CuO/Al nanothermite materials.

Mixing method	Flame speed (m/s)	Pressure speed (m/s)	Pressure mach no.
Physical mixing	1500 ± 250	766 ± 8.1	2.25
Self-assembly	2200 ± 300	831 ± 44.4	2.44

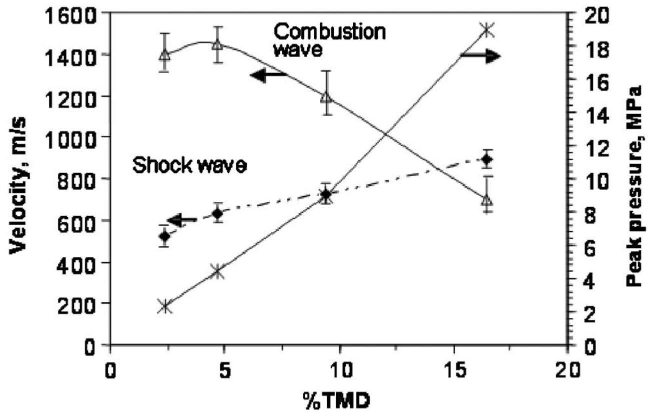

FIG. 4. Plot of combustion velocity, shock wave velocity, and peak pressure as a function of the density of physically mixed CuO/Al composite.

typical nanorod composites, the density is usually low (%TMD varies from 2% to 16%) and the combustion wave velocity is in the range of 1500–2300 m/s.[6] From the law of conservation and continuum mechanics, the CJ pressure (P_{cj}) in gigapascals can be calculated using the relation

$$P_{\mathrm{cj}} = \rho D^2/(\gamma + 1), \qquad (2)$$

where γ is the negative slope of the isentrope, ρ is the density in g/cm^3, and D is the detonation velocity in km/s. For our nanothermites, assuming that the reaction products vaporize instantaneously at the very high temperature, we take γ of the gas-air mixture as 1.4, ρ as 0.001 18 g/cm^3, and typical D as 2 km/s; then, we obtain the CJ pressure as 1.97 MPa, which is of the same order as the peak pressure obtained experimentally [Fig. 3(b)]. It is understood that this assumption of instant vaporization is not accurate, and development of an equation of state is needed for numerical simulation studies of nanothermite materials. For solid explosives, the CJ theory, although it assumes the chemical reaction to happen instantaneously, predicts the experimental detonation velocity well.

Thus, we make an effort to correlate the peak pressure and detonation velocity for a few samples of our nanothermites according to the CJ theory. Figure 5 shows a plot of peak pressure P vs ρD^2 for a range of densities for which the detonation velocity is above 1 km/s. Using the slope of the curve as $m = 1/(\gamma+1)$, we get an approximate value of γ as 59 according to the continuum theory. The discrepancy of this value from the solid explosive, for which $\gamma=3$, may be attributed to low density multiphase nature of the nanothermite materials and limitations of continuum theory in the timescale of our interest. In our future work, we plan to develop a more realistic numerical model in suitable timescale based on molecular dynamics simulation.

In conclusion, we have demonstrated that the fast propagating combustion of CuO/Al nanothermites could generate shock waves with potential applications in various fields. In the future, we will conduct an integrated analytical, experimental, and numerical study to develop a realistic model for the combustion process with the use of both continuum and molecular level approaches.

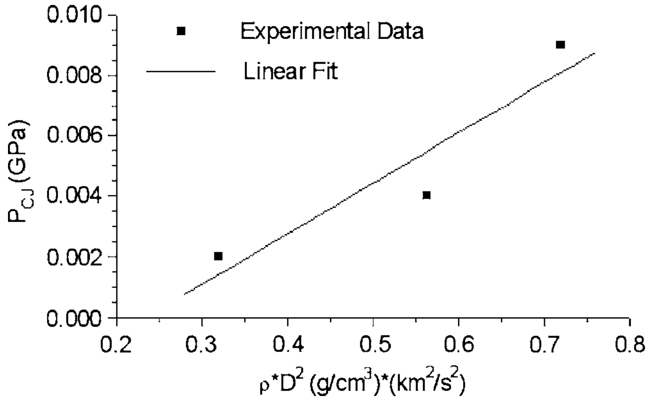

FIG. 5. Plot of CJ pressure vs ρD^2 used to determine the experimental value for γ.

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