Combustion and Flame 158 (2011) 1084–1088

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Enabling and controlling slow reaction velocities in low-density compacts of multilayer reactive particles

Gregory M. Fritz *, Howie Joress, Timothy P. Weihs

Department of Materials Science and Engineering, The Johns Hopkins University, 3400 N. Charles St., 206 Maryland Hall, Baltimore, MD 21218, USA

ARTICLE INFO

Article history:
Received 3 August 2010
Received in revised form 26 September 2010
Accepted 11 October 2010
Available online 11 November 2010

Keywords:
Energetic material
Multilayer particle
Hierarchical structures
Reaction velocity
Reactive nanomaterial

ABSTRACT

Uniformly-shaped, micron-scale particles with nanoscale layers of Al and Ni and a volume fill of 20% ± 1% were fabricated by depositing Al/Ni multilayer films onto mesh substrates with a square weave. The films break into individual particles at the weave intersections during removal and the resulting particles have lengths equal to three times their widths. Exothermic formation reactions in loose compacts of these particles were shown to self-propagate up to 200 times slower than reactions in continuous multilayer foils with similar chemistries, layer thicknesses and ignition thresholds. The difference is attributed to the time delay associated with heating each subsequent particle to the point of ignition as the reaction propagates. The results presented here demonstrate an ability to separately control the rate of mass diffusion and the rate of thermal diffusion in particle compacts and thereby produce slow and stable self-propagating formation reactions. Such reactions are desirable for both industrial and military applications such as chemical time delays.

1. Introduction

Interest in novel energetic materials that react by deflagration has grown significantly over the last decade for applications including decoy flares [1], chemical time delays [2], thermal batteries [3], advanced intermetallic or foam synthesis [4,5], heat sources for joining [6], and neutralization of chemical and biological weapons [7]. Most of these energetic materials enable simple formation reactions such as $Al + Ni \rightarrow AlNi$ or slightly more complex reduction–oxidation reactions such as $2Fe + Al_2O_3 \rightarrow Fe_2O_3 + 2Al$. The materials can be fabricated as compacts of powders [8–10], core–shell particles [11–13], or nanolayered foils [14–19], and their reactions produce rapid bursts of heat and light with maximum temperatures above 1500 °C [20]. Initiation thresholds and deflagration rates can be controlled by varying the scale or spacing of the reactants from the 10's of microns seen in tradition powder compacts down to the 10's of nanometers now achieved in novel, nanoenergetic materials [17–22]. For example, in a fully dense Al/Ni multilayer foil the rate of deflagration increases approximately 200 times as the reactant spacing decreases from 1000 nm to 20 nm; the rise is attributed to the drop in reactant spacing and the corresponding shorter time needed to complete diffusive mixing of the reactants [18]. For certain applications such as chemical time delays and neutralization of biological or chemical weapons, slow deflagration rates are beneficial. However, a slow propagation rate dramatically increases the risk of quenching in dense energetic materials as the rate of heat losses to the material ahead of the reaction front can exceed the rate of heat generation within the reaction front [24,25].

In compacts of conventional elemental reactant powders, the particle size and packing density control both the mass transport and the thermal transport within the energetic material. Thus, the rate at which heat is generated due to reactant intermixing cannot be controlled independently from the rate at which heat is conducted into neighboring particles. In fully dense multilayer foils, the rate of intermixing can be varied in a controlled manner by altering the reactant layer thickness but the rate of heat dissipation along a foil is relatively constant for a given average chemistry. In addition, thermal conduction is typically too high to produce slow and steady reaction velocities in multilayer foils [26]. To develop slow reactions, one desires an energetic material wherein the physical parameters that control mass transport are decoupled from those that control thermal transport and hence can be studied and optimized independently. Here we demonstrate such a novel material through the fabrication of microscale particles with nanoscale layers of reactants, and we report very slow deflagration reactions with no signs of quenching.

2. Experimental

2.1. Multilayer particle fabrication

Multilayer Al/Ni particles were deposited by DC magnetron sputtering from Al 1100 alloy [99 wt.% Al, 0.87 wt.% (Si, Fe),

---

* Corresponding author.
E-mail address: greg.fritz@jhu.edu (G.M. Fritz).

0010-2180/$ - see front matter
doi:10.1016/j.combustflame.2010.10.008

0.12 wt.% Cu] and Ni alloy [93 wt.% Ni, 7 wt.% V] targets at 2.65 and 1.66 W/cm^2, respectively. Vanadium was included in the Ni sputter target to make it nonmagnetic and thus allow for faster and more stable deposition. The relative thickness of Al and Ni layers was maintained at a 3:2 ratio in order to obtain particles with an average stoichiometry of $Al_{50}Ni_{46}V_4$. The nanolayered particles were deposited in 1 mTorr of 99.999% pure argon in a vacuum chamber with a base pressure of less than 4×10^{-6} Torr. The substrates were square nylon meshes with 50 μm fiber diameters and they were used as-received from Ecologix Environmental Systems, LLC (Fig. 1a). The particles were removed from the mesh substrates by folding and rubbing the nylon against itself under water to prevent the particles from becoming airborne and to reduce any risk of ignition. The water-particle slurry was then filtered through a series of ASTM filters to separate matter larger than the particles' length and smaller than the particles' width from the particles themselves. The particles were then air dried before being collected. Care was taken to not subject the particles to elevated temperatures in order to prevent intermixing of the reactants. Optical and scanning electron micrographs (Fig. 1b) show that the particles are highly uniform in geometry and size and can be considered discontinuous, curved pieces of multilayer foil.

2.2. Calorimetry

The heats of reaction for multilayer foils and particles were measured in a Perkin Elmer Pyris 1 Differential Scanning Calorimeter (DSC). In each scan, 5–15 mg of reactive material were heated from 50 °C to 720 °C at 40 °C min^{-1} in an atmosphere of 99.999% pure argon flowing at 20 mL min^{-1}. The heat of reaction is equivalent to the energy released as heat during the complete chemical reaction of a given sample and was measured by performing two heating scans: one with the as-deposited material and a second one with the same material after a brief cool-down. The second scan serves as a baseline scan and the heat of reaction was calculated by integrating the difference of the two scans [27].

2.3. Reaction velocity measurement

The as-fabricated particles were funneled into glass tubes with an inside diameter of 4 mm ± 0.5 mm, lengths ranging from 20 mm to 30 mm, and a wall thickness of 1.2 mm. The bottom of the tube was capped with a rubber plug and a silicone cap while the top was left open. The glass tube was then placed vertically into a small vacuum chamber where a mechanical pump was used to obtain a base pressure of ~100 mTorr. A nichrome filament was placed in contact with the top of the particle compact and was heated with a pulse of current for approximately 0.5 s in order to initiate the reaction. A Sony Handycam HDR-CX7 with 120 frames per second resolution recorded the reaction front traveling downward and Vegas Movie Studio Platinum 9.0 was used to analyze the frames and determine the reaction velocity.

2.4. Ignition threshold measurement

The ignition temperatures for foils and particles with various layer thicknesses were obtained by dropping the energetic materials upon a grounded hot plate held at a constant temperature. The hot plate temperature was increased until the energetic materials ignited when dropped on its surface. After being dropped onto the hot plate once, the particles were discarded and fresh material was used for the subsequent test. Two thermocouples were used to determine the temperature of the hot plate: one inside the hot plate and one on the top surface. Both thermocouples displayed the same temperature within 1 °C before an ignition experiment was performed. The hot plate used for these experiments was CER-1-01 from Watlow: a resistively-heated aluminum nitride block with a smooth surface.

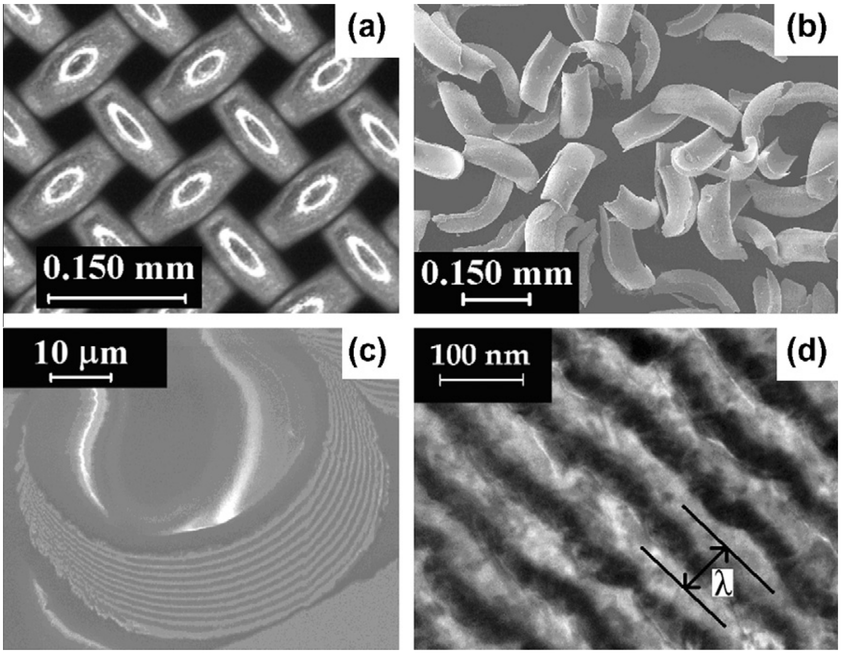

Fig. 1. (a) Nanolayered particles are fabricated by sputtering onto a rotating nylon mesh with a square weave where the wire diameter is equal to the mesh opening. (b) The particles break at the weave intersections during removal so that the particle length is three times the particle width for all particles. (c) The layers within a particle vary due to the curvature of the woven fibers. The maximum bilayer for the particle seen here is 1.5 μm and the volume-averaged bilayer spacing is 1.2 μm. (d) A cross-sectional TEM micrograph of the bilayers (λ) of a particle with a maximum bilayer spacing of 105 nm and a volume-averaged bilayer spacing of 87 nm. The bilayers seen here are approximately 68 nm.