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Ignition studies of Al/Fe_2O_3 energetic nanocomposites

L. Menon,[a] S. Patibandla, K. Bhargava Ram, S. I. Shkuratov, D. Aurongzeb, and M. Holtz
Department of Physics and Nanotech Center, Texas Tech University, Lubbock, Texas 79409

J. Berg
Department of Mechanical Engineering and Nanotech Center, Texas Tech University, Lubbock, Texas 79409

J. Yun and H. Temkin
Department of Electrical Engineering and Nanotech Center, Texas Tech University, Lubbock, Texas 79409

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We prepare energetic nanocomposites, which undergo an exothermic reaction when ignited at moderate temperature. The nanocomposites are a mixture of Al fuel and Fe_2O_3 oxidizer where Fe_2O_3 is in the form of an array of nanowires embedded in the thin Al film. We achieve a very high packing density of the nanocomposites, precise control of oxidizer–fuel sizes at the nanoscale level, and direct contact between oxidizer and fuel. We find that the flame temperature does not depend on ignition temperature. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1759387]

Energetic materials[1,2] are a class of substances that store energy chemically and, when ignited, undergo an exothermic reaction without the need for an external substance such as oxygen. Traditionally, fabrication of such materials has involved processes such as grinding and mixing oxidizer and fuel components (as in black powder) or the introduction of oxidizer and fuel into one molecule (as in trinitrotoluene). Nanoscaled energetic composites, due to increased surface to volume ratio of the reactants, can result in higher-energy release in comparison with traditional materials. In this regard, two processes to prepare such nanocomposites are being developed, namely, sol–gel processing and multilayered foils. Sol–gel chemistry produces nanometer-size particles immersed in a solid network.[3] Such structures are macroscopically uniform due to the small particle size and the small interparticle separations. However, the particle distribution is random which can inhibit self-sustaining processes by locally separating the fuel and oxidizer. In addition, sol–gel reactants often have organic impurities that make up about 10% of the sample mass.[4] These factors result in reduced energy release. Multilayered foils consisting of alternating layers of oxidizer and fuel material provide large, regular planar interfaces and very close physical contact between oxidizer and fuel reactants.[5,6] They are nanoscaled in one dimension and the energy release proceeds through interdiffusion at the interface.

We demonstrate a fabrication approach to prepare energetic nanocomposites based on advanced nanoengineering and processing methods. Our composites are highly structured consisting of an array of nanowires partially embedded in a thin film. The wires are perpendicular to the film allowing for the maximum possible density of the nanowires. Our approach allows precise control of the oxidizer and fuel structure for achieving excellent physical contact.

Oxidizer nanowires are formed in a regular array by self-assembly, and embedded in the fuel by means of thin-film deposition. The nanowires are prepared using nanoporous alumina membranes.[7–9] Fabrication of the membranes involves dc electrochemical anodization of an aluminum foil in an acid. During anodization, aluminum is converted to nanoporous aluminum oxide. The diameter of the pores is controlled by the anodization voltage and the acid used. Typical pore diameters range from 8 to 200 nm. Figure 1(a) shows the top view image of a nanoporous alumina template with pore diameter 50 nm. The image demonstrates the high level of ordering obtained for these templates. The pores do not reach the aluminum surface [see schematic diagram in Fig. 1(b)] due to the presence of a 30 to 40 nm thick barrier layer of aluminum oxide at the bottom of the pores. Presence of this barrier layer is sufficient to inhibit interdiffusional reaction between the aluminum and an oxidizer (Fe_2O_3).[10,4] Once the templates are synthesized, nanowire arrays can be prepared by ac electrodeposition[11–13] inside the pores [see Fig. 1(b)]. Length of the wires can be controlled by adjusting the time of deposition. Figure 1(c) shows a typical cross-section scanning electron microscopy (SEM) image demonstrating nanowires arranged in a parallel manner inside nanoporous alumina templates.

A schematic illustration of the approach developed here for fabricating such nanocomposites is shown in Fig. 2. Fe nanowires are electrodeposited into nanoporous alumina templates (steps I–III). The electrodeposited sample is then coated with a thin organic layer (step IV) followed by soaking in 3% mercuric chloride solution (step V) to remove the Al layer at the bottom. The organic layer protects the Fe wires inside the pores from being etched away by mercuric chloride solution during this process. In the next step, the organic layer is removed in ethyl alcohol solution (step VI) and the sample is dried. The sample is soaked in a mixture of chromic-phosphoric acid at 60 °C to partially etch the pores from the top (step VII), revealing Fe wires. At this stage, the exposed part of the Fe nanowires, are oxidized. The sample is rinsed and dried and a thin film of Al (50 nm) is coated on top by means of thermal evaporation (step VIII). Al film is now in contact with Fe/Fe_2O_3 nanowires. The sample is briefly annealed at 100 °C to further improve the interface contact between Al and the nanowires. It is then soaked in

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[a] Electronic mail: latika.menon@ttu.edu

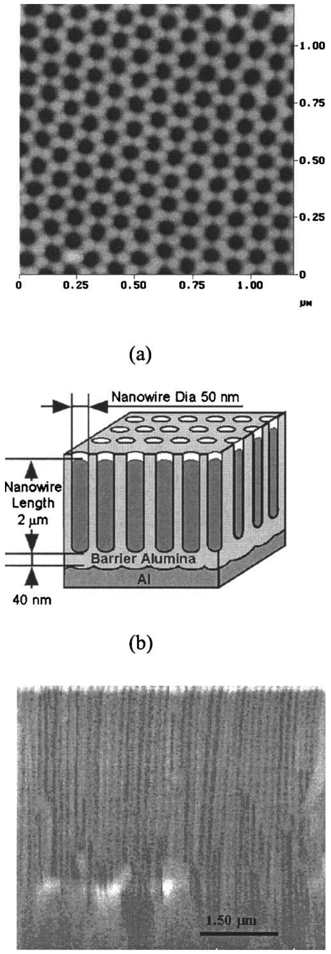

FIG. 1. (a). AFM image of a nanoporous alumina template fabricated by anodization in 3% oxalic acid at 40 V. The dark areas are the pores while the light areas are the surrounding aluminum oxide. The pore diameter is about 50 nm. (b) Schematic diagram of a nanoporous alumina template containing deposited nanowires. (c) Cross-section SEM image of a nanoporous alumina template containing electrodeposited nanowires.

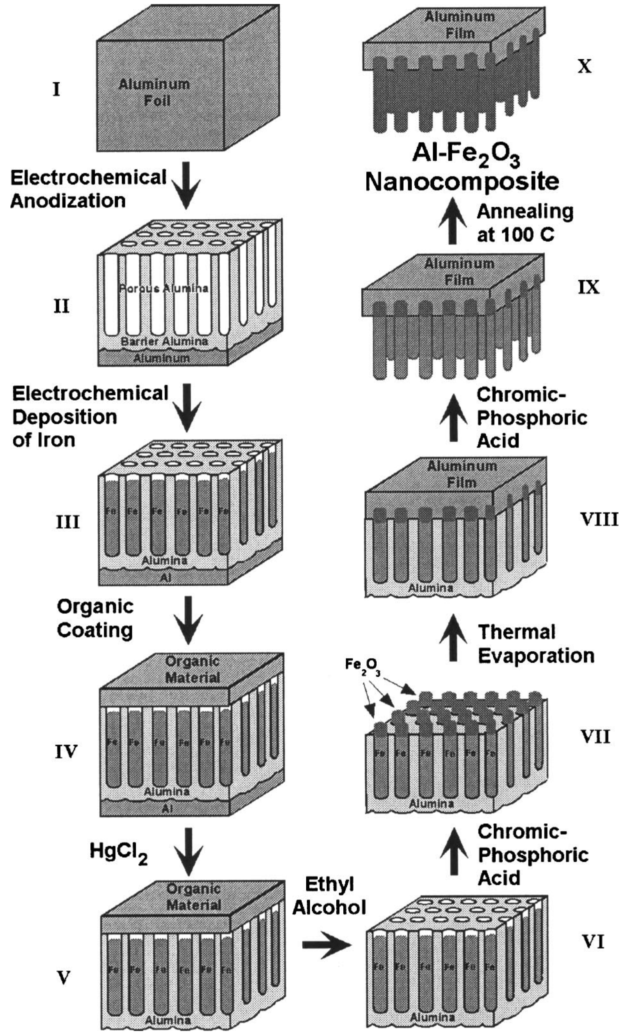

FIG. 2. Sequence of steps to prepare energetic nanocomposites.

chromic–phosphoric acid mixture (step IX) to etch away the remaining aluminum oxide film. At this stage, all of the Fe wires are converted to Fe oxide. The sample is cleaned, dried, and annealed (step X) to completely remove trace amounts of water vapor.

A typical SEM image of a high-density nanowire array embedded in Al film is shown in Fig. 3. The diameter of a single nanowire is about 50 nm and the density of nanowires for all observed specimens is $\sim 10^{10}$ wires/cm^2.

For maximum energy density, one would like to fabricate samples having controlled size of fuel and oxidizer at the nanoscale level and intimate physical contact between fuel and oxidizer. These conditions are satisfied using our approach. In our samples, the reactive part of the specimen is the portion of Fe$_2$O$_3$ nanowire embedded in the Al film (Fig. 2X). Fe$_2$O$_3$ is in effect covered with aluminum layer of thickness 25 nm. In this sense, our sample consists of an array of nanowires in a closely packed arrangement. Sizes of fuel and oxidizer can be controlled in our fabrication procedure. This is because the diameter of the wires depends only on the pore diameter of the nanoporous alumina membranes. The close physical contact between fuel and oxidizer is a result of direct vacuum deposition of the Al film on the nanoarray. This approach eliminates the formation of an aluminum oxide barrier at the Al/Fe$_2$O$_3$ interface during deposition. Close packing of the embedded nanowires tips results in the high density of 10^{10} cm^{-2} and a surface fill factor of 0.2.

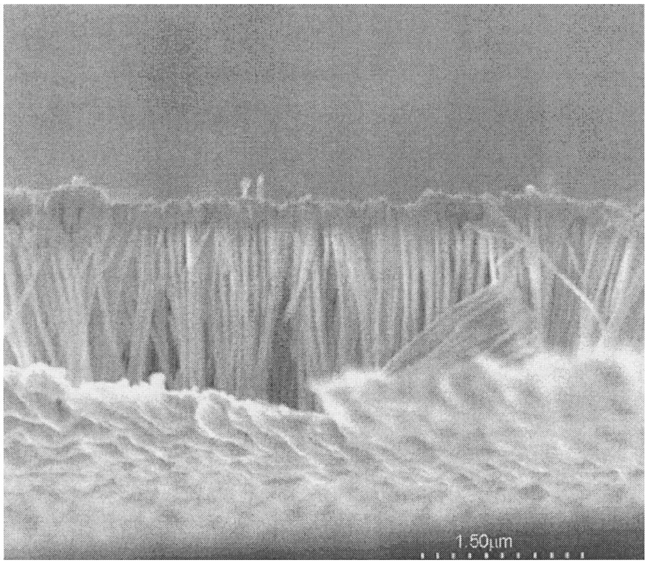

FIG. 3. SEM image showing the cross section of the fabricated Al/Fe$_2$O$_3$ nanocomposite.

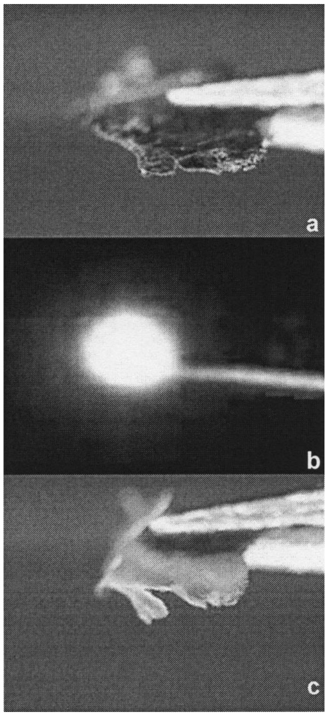

FIG. 4. (a) Image of energetic sample before ignition (size is of the order of millimeters), (b) bright flash of light as demonstrate by an igniting sample, and (c) image of sample after ignition.

Ignition has been achieved using a butane flame, resistive heating element, and laser illumination. Figure 4(b) shows an image of an igniting sample using an electrically heated filament. Before and after ignition images are also shown for comparison in Figs. 4(a) and 4(c). The temperature of the heating wire is calibrated using an optical pyrometer. Ignition temperatures are well below the Al melting point of 660 °C. Ignition is accompanied by a bright flash of light. The reaction temperature is obtained by measuring the blackbody emission spectrum of the igniting sample. Figure 5 shows the plot of flame temperature as a function of ignition temperature. Ignition starts at a temperature of ~410 °C. As expected, the flame temperature is independent of the ignition temperature and is of the order of 4000 °C. The high flame temperature is consistent with the large energy release expected. The flame temperature in our samples may be compared with the reported "adiabatic flame temperature" of about 3250 °C for the Al–Fe_2O_3 reaction.[14]

The thermite reaction between aluminum and iron oxide can be written as

$$Fe_2O_3 + Al \rightarrow Fe + Al_2O_3 + \Delta H, \qquad (1)$$

where ΔH is the energy released during the reaction. We estimate the amount of energy released per square centimeter of our samples using the following known values from literature (heat of formation for Al_2O_3 is −335 kJ/mole atom and heat of formation for Fe_2O_3 is −168 kJ/mole atom).[15] Assuming a volume reaction between Fe_2O_3 and Al, we estimate that the energy released is about 0.4 J/cm^2. This is a thousand times higher than the energy released due to a purely surface reaction (as in planar films).

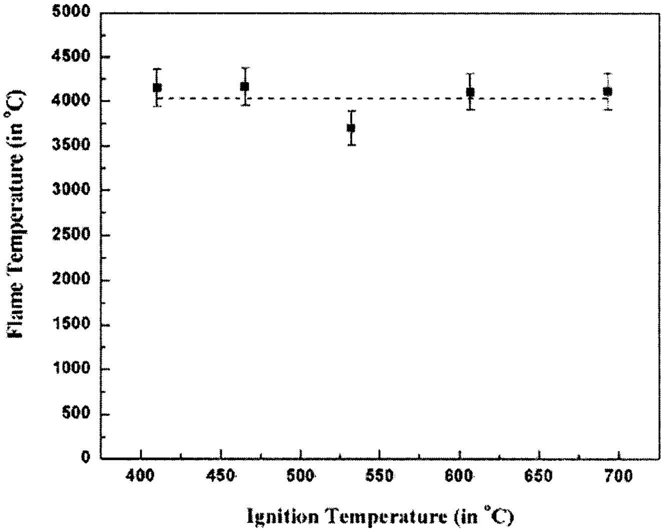

FIG. 5. Flame temperature as a function of ignition temperature for Al–Fe_2O_3 nanocomposites.

In conclusion, we describe a highly reproducible approach to create high-energy density composites. The advantage of this technique is precise control of oxidizer and fuel dimensions at the nanometer scale. The method precludes both the incorporation of impurities and the oxidation of the aluminum at the fuel–oxidizer interface prior to ignition. Ignition temperatures are well below the melting point of aluminum, while reaction temperatures are high (~4000 °C) and independent of ignition temperature.

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