Size dependence of energetic properties in nanowire-based energetic materials

L. Menon,a) D. Aurongzeb, S. Patibandla, and K. Bhargava Ram
Department of Physics, Texas Tech University, Lubbock, Texas 79409 and Nanotech Center,
Texas Tech University, Lubbock, Texas 79409

C. Richter and A Sacco, Jr.
Center for Advanced Microgravity Materials Processing, Department of Chemical Engineering,
Northeastern University, Boston, Massachusetts 02115

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We prepared nanowire-array-based thin film energetic nanocomposites based on Al–Fe2O3. The ignition properties as a function of wire dimensions and interwire spacing have been investigated. We show significant variations in ignition behavior, which we relate to the kinetic and heat transfer dynamics of the various configurations studied. Our results indicate the possibility for nanoscale control of reaction parameters such as flame temperature and burn rate in such composites for optimized configurations (optimum wire size, interwire spacing, film thickness, etc.). © 2006 American Institute of Physics. [DOI: 10.1063/1.2234551]

I. INTRODUCTION

Recently, we demonstrated a nanocomposite material, which exhibits ignition at moderate temperatures.1 The material is a mixture of oxidizer and fuel and is in the form of a nanowire-array-based thin film. In our demonstration, we focused on the fabrication of Al–Fe2O3 based nanocomposites. Fe2O3 (oxidizer) is in the form of nanowires embedded vertically in a thin Al (fuel) film. The unique features of our nanocomposites are their highly structured nature and tight packing, intimate mechanical contact between oxidizer and fuel components, and precisely controlled oxidizer-fuel sizes and positions at the nanometer scale. Such nanocomposites have several potential applications in energy sources, microelectromechanical system (MEMS)-based energetic devices, etc. More importantly, our samples are model systems in which we can study fundamental properties of energetic phenomena at the nanoscale level. In this paper, we have studied the ignition properties of the nanocomposite as a function of oxidizer-fuel sizes and nanocomposite spacing.

First, a brief background is given to the fabrication of the nanocomposite. Fe nanowires are created in a regular array by means of ac electrodeposition inside nanoporous alumina membranes. The sample is then coated with a thin organic layer followed by soaking in 3% mercuric chloride solution to remove the Al layer at the bottom. During this process, the top organic layer protects the Fe inside the pores from being etched away by mercuric chloride solution. In the next step, the organic layer is removed in ethyl alcohol. The sample is soaked in a mixture of chromic-phosphoric acid at 60 °C to partially etch the pores from the top, revealing Fe wires. At this stage, the exposed part of the Fe nanowires is oxidized to Fe oxide. The sample is rinsed and dried and a thin Al film (thickness ~50 nm) is thermally evaporated on the surface of the nanowire array. Al film is now in direct contact with Fe/Fe oxide nanowires. The sample is annealed at 100 °C for a few minutes in order to improve the interface contact between Al and the nanowires. It is then soaked in chromic-phosphoric acid mixture to etch away the remaining alumina template around the wires. At this stage all of the Fe wires are converted to Fe oxide. This leaves behind an Al film attached to an array of Fe oxide nanowires. The sample is cleaned, dried, and annealed to completely remove trace amounts of water vapor. A typical cross-section scanning electron microscopy image of the final product is shown in Fig. 1. In the image, the diameter of a single nanowire is about 50 nm and the density of nanowires for all observed specimens is 1010 wires/cm2 with a surface fill factor of 0.2. In our fabrication approach, the size of fuel and oxidizer can be easily controlled. The smallest achievable wire diameter is of the order of 10 nm and the largest packing density that we can obtain is of the order of 1011 wires/cm2. The method may also be modified to fabricate fuel nanowire arrays embedded in oxidizer films.

II. EXPERIMENTAL DETAILS

In this study, we have restricted ourselves to investigating the ignition behavior of nanocomposites as shown in Fig. 1, with Fe2O3 nanowires embedded in a thin Al film. We

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a)Author to whom correspondence should be addressed; electronic mail: l.menon@neu.edu

FIG. 1. Cross-section scanning electron microscopy image showing the array of Fe2O3 nanowires embedded in an Al film.
prepared samples with two different diameters of the Fe₃O₄ nanowire, namely, 50 and 10 nm. The length of the wire is of the order of 2 μm. The thickness of the Al film is of the order of the thickness of 50 nm in both samples. The schematic diagram showing the cross-section image of the sample is shown in Figs. 2(a) and 2(b). For the sample with 50 nm diameter wires, the interwire separation is ~100 nm, and for the sample with 10 nm diameter wires, the interwire separation is ~60 nm.

III. RESULTS AND DISCUSSIONS

The nanocomposites are ignited in air using an electrically heated filament. A regulated dc power source is used to heat a nichrome wire and the temperature of the heating wire is calibrated using a thermocouple. The samples are brought in contact with the heated filament. At the point of ignition, the temperature of the filament is found to be around 410 °C, well below the Al melting point of 660 °C. For the nanocomposite with 50 nm diameter wires, a bright flash of light is observed. In the case of the nanocomposite with 10 nm diameter wires, instead of a bright flash of light, a slowly propagating light spark is observed. Thus, there is a difference in reaction propagation for these samples as a function of wire diameter. This behavior will be discussed below.

Ignition for the structured sample with 50 nm diameter oxidizer nanowires is first discussed. As mentioned above, ignition is accompanied by a bright flash of light. The temperature of the flame was measured by means of an optical spectrometer. The blackbody spectrum of the flame is recorded and temperature of the flame is calculated by applying Wien’s law (λ_maxT=0.3 cm K). From this we determine that the flame temperature of the sample is independent of ignition temperature (as expected) and is of the order of 4000 °C. Figure 3(a) shows the plot of flame temperature versus ignition temperature for these samples.

It is interesting to study the dependence of flame temperature on thickness of Al film. For this we prepared a new set of samples with a higher Al film thickness of 120 nm. As before, the flame temperature is found to be independent of ignition temperature and the average value is ~3785 °C [see Fig. 3(b)]. These values are slightly lower than the measured 4000 °C for the samples with 50 nm thick Al film and may be attributed to conductive heat loss through the excess Al below the nanowires (discussed below). It must also be added that this value is within experimental margin of error (±200 °C) for this measurement. As an additional investigation, we measured the flame temperature as a function of wire length. We prepared a new set of samples with wire length of the order of 0.5 μm and Al film thickness of the order of 50 nm. Again, we do not observe a strong dependence on wire length. The average flame temperature is about 4046 °C. Subsequently we conclude that the flame temperature in our samples is in the range of ~4000 °C for most sample configurations given a wire diameter fixed at 50 nm.

The observed flame temperature may be compared with the adiabatic flame temperature for the Al–Fe₃O₄ reaction. In the case of Al–Fe₃O₄, the complete reaction can be written as follows:

\[ \text{Fe}_3\text{O}_4 + 2\text{Al} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3 + \Delta H, \]

where \( \Delta H \) is the heat of reaction and is of the order of 850 kJ/mole.

Assuming there is no heat loss (radiation losses, etc.,), one can write

\[ \Delta H = C_{P,\text{Fe}_3\text{O}_4} \Delta T_1 + C_{P,\text{Al}} \Delta T_1 + \sum \lambda_i. \]

Here, \( C_P \) is the appropriate specific heats of the products, \( \Delta T_1 = T_f - T_i \) is the adiabatic temperature increase (\( T_i \) is the initial temperature of the sample and \( T_f \) the adiabatic flame temperature), and \( \sum \lambda_i \) denote the latent heat of all phase transitions.
transitions of the reactants between \( T_f \) and \( T_i \). From the above calculation, an adiabatic flame temperature of \( \sim 3250 \, ^\circ\text{C} \) for the stoichiometric Al–Fe\(_2\)O\(_3\) reaction is obtained.\(^{1,3}\) The measured flame temperature of \( 4000 \, ^\circ\text{C} \) in our samples is thus much higher than the adiabatic flame temperature of \( 3250 \, ^\circ\text{C} \). There are several possible theories that can explain this effect as will be discussed below.

One possible explanation for the large flame temperature is the possibility of a nonequilibrium situation wherein there is preheating in a small region at the interface. The steady propagation of the reaction involves conductive (or radiative) preheating of the reactants ahead of the reaction front. This preheating may, in the highly nonequilibrium setting of these ultrafast reactions, be to a level that is high enough to account for the observed ignition flame temperature. In fact, Brewster\(^4\) has observed similar high flame temperatures for powder samples and believe that it is a result of radiative preheating or “heat feedback.” We are currently developing an appropriate model\(^5\) for our unique samples which will explore this effect further.

It must be emphasized that the thermite reaction in our samples occurs at the interface of the two reactants (see reaction zone in Fig. 2). Thus only a small region of the Fe\(_2\)O\(_3\) at the bottom end of the nanowire reacts with the Al around it (consistent with our observation that flame temperature does not depend on wire length). Hence, the remaining Fe\(_2\)O\(_3\) (almost the entire length of the nanowire) and a small amount of Al in the intermediate region between two wires are in excess. A possible explanation for the large flame temperature could be the reaction of the excess Al with oxygen in the air leading to an additional energy source. Theoretically this could occur if the “Glassman criterion”\(^6\) is met, that is, if the aluminum film surface (unreacted Al situated close to reaction zone) temperature exceeds the Al\(_2\)O\(_3\) melting point (\( \sim 2000 \, ^\circ\text{C} \)). The combustion of oxygen and aluminum has a significantly higher flame temperature which can result in the large observed flame temperature. This would be an interesting effect with significant implications. Our samples could be used in applications involving nanoscaled, ultrafast high temperature synthesis. Nanomaterials that would otherwise require very high temperature for their production can be prepared very easily by incorporating them appropriately with the energetic material. It is important to note that for the Glassman criterion to be satisfied, the right amount of Al must be situated close to the reaction zone. Otherwise, the excess Al will in contrast function as a conductive heat sink as will be discussed below.

Based on the above analysis, we can now explain the absence of a light flash for the structured sample with 10 nm diameter oxidizer nanowires. For these wires, the reaction volume for Fe\(_2\)O\(_3\) at the interface is much smaller [see Fig. 2(b)]. However, the interwire separation is very large \( \sim 60 \, \text{nm} \). Therefore there is a large amount of unreacted aluminum in the array between any two iron oxide nanowires. The unreacted Al results in conductive heat losses in the sample and a large drop in reaction velocity. Melting of Al at \( \sim 660 \, ^\circ\text{C} \) will lead to further reduction in reaction velocity. This explains the slowly propagating spark observed during the ignition of these samples. The specific heat of aluminum is known from literature to be \( \sim 1000 \, \text{J/kg K} \) at around \( 300–400 \, ^\circ\text{C} \). Therefore, it is also possible that the reaction will be quenched in samples with configurations where insufficient heat is evolved by the reaction to make up for the heat sink (of excess Al).\(^7,8\)

IV. CONCLUSION

We have shown that the ignition properties of the nanowire-based nanocomposite strongly depend on the dimensions and spacing of the nanocomposite. For samples with wire diameter 50 nm ignition is accompanied by a bright flash of light. On the other hand for samples with wire diameter of 10 nm, instead of a bright flash of light one observes a slowly propagating light spark. The difference in behavior is attributed to conductive heat losses through excess Al in the smaller wire samples. We also observe a very large flame temperature for the samples with 50 nm diameter wires. This large flame temperature is higher than the theoretical adiabatic flame temperature. This is suggestive either of highly nonequilibrium heat transfer in our samples or due to the additional energy source of aluminum combustion with air.

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\(^1\)L. Menon et al., Appl. Phys. Lett. 84, 4735 (2004).


