



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Formulation and Performance of Novel Energetic Nanocomposites and Gas Generators Prepared by Sol-Gel Methods

B. J. Clapsaddle, L. Zhao, D. Prentice, M. L. Pantoya,
A. E. Gash, J. H. Satcher Jr., K. J. Shea, R. L. Simpson

March 25, 2005

36th Annual Conference of ICT
Karlsruhe, Germany
June 28, 2005 through July 1, 2005

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

FORMULATION AND PERFORMANCE OF NOVEL ENERGETIC NANOCOMPOSITES AND GAS GENERATORS PREPARED BY SOL-GEL METHODS

Brady J. Clapsaddle¹, Lihua Zhao², Daniel Prentice³, Michelle L. Pantoya³, Alexander E. Gash¹, Joe H. Satcher Jr.¹, Kenneth J. Shea², and Randall L. Simpson¹

¹. Lawrence Livermore National Laboratory, 7000 East Ave., L-092, Livermore, California, U.S.A.

². University of California - Irvine, Irvine, California, U.S.A.

³. Texas Tech University, Lubbock, Texas, U.S.A.

ABSTRACT

In the field of composite energetic materials, properties such as ingredient distribution, particle size, and morphology affect both sensitivity and performance. Since the reaction kinetics of composite energetic materials are typically controlled by the mass transport rates between reactants, one would anticipate new and potentially exceptional performance from energetic nanocomposites. We have developed a new method of making nanostructured energetic materials, specifically explosives, propellants, and pyrotechnics, using sol-gel chemistry. A novel sol-gel approach has proven successful in preparing nanostructured metal oxide materials. By introducing a fuel metal, such as aluminum, into the nanostructured metal oxide matrix, energetic materials based on thermite reactions can be fabricated. Two of the metal oxides are tungsten trioxide and iron(III) oxide, both of which are of interest in the field of energetic materials. Due to the versatility of the preparation method, binary oxidizing phases can also be prepared, thus enabling a potential means of controlling the energetic properties of the subsequent nanocomposites. Furthermore, organic additives can also be easily introduced into the nanocomposites for the production of nanostructured gas generators. The resulting nanoscale distribution of all the ingredients displays energetic properties not seen in its micro-scale counterparts due to the expected increase of mass transport rates between the reactants. The unique synthesis methodology, formulations, and performance of these materials will be presented. The degree of control over the burning rate of these nanocomposites afforded by the compositional variation of a binary oxidizing phase will also be discussed. These energetic nanocomposites have the potential for releasing controlled amounts of energy at a controlled rate. Due to the versatility of the synthesis method, a large number of compositions and physical properties can be

achieved, resulting in energetic nanocomposites that can be fabricated to meet specific safety and environmental considerations.

INTRODUCTION

Since the invention of black powder, one thousand years ago, the technology for making solid energetic materials has remained either the physical mixing of solid oxidizers and fuels (e.g. black powder), or the incorporation of oxidizing and fuel moieties into one molecule (e.g., trinitrotoluene (TNT)). The basic distinctions between these energetic composites and energetic materials made from monomolecular approaches are as follows. In composite systems, desired energy properties can be attained through readily varied ratios of oxidizer and fuels. A complete balance between the oxidizer and fuel may be reached to maximize energy density. However, due to the granular nature of composite energetic materials, reaction kinetics are typically controlled by the mass transport rates between reactants. Hence, although composites may have extreme energy densities, the release rate of that energy is below that which may be attained in a chemical kinetics controlled process. In monomolecular energetic materials the rate of energy release is primarily controlled by chemical kinetics, and not by mass transport. Therefore, monomolecular materials can have much greater power than composite energetic materials. A major limitation with these materials is the total energy density achievable. Therefore, it is desirable to combine the excellent thermodynamics of composite energetic materials with the rapid kinetics of the monomolecular energetic materials. One possible way to do this is to mix the components of composite energetic materials on a size scale which will limit the effects of mass transport on the reactants, thus providing kinetics similar to those obtained in monomolecular energetic materials.

We have previously prepared pyrotechnic and explosive composites based on thermite reactions whose fuel and oxidizer constituents are intimately mixed on the nanometer-sized scale [1-5]. These energetic nanocomposites, in an attempt to prepare a high energy, high power energetic nanocomposite with controlled burning properties, are prepared by taking advantage of the unique nanoarchitecture and mixing properties provided by sol-gel chemistry. In addition, sol-gel chemistry has also allowed for organic gas generants to be “stitched” into the nanocomposite matrix. This paper will discuss the performance of energetic nanocomposites containing $\text{Fe}_2\text{O}_3\text{-SiO}_2$ binary oxidizing phases. Thermite nanocomposites have been prepared by mixing aluminum nanoparticles with both commercial $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanopowders and sol-gel prepared $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanopowders. The effect of these two synthesis and mixing techniques on the

burning rates of the resulting thermites will be discussed. Finally, thermites containing binary oxidizing phases that incorporate organic functionality for gas generation will be evaluated.

EXPERIMENTAL DETAILS

Synthesis of Fe₂O₃-SiO₂ and Fe₂O₃-organic functionalized SiO₂ (Fe₂O₃-SiO_{3/2}-R) nanocomposites

Nanocomposites were prepared for Fe₂O₃-SiO₂ oxidizers and Fe₂O₃-SiO_{3/2}-R oxidizers (R = -(CH₂)₂(CF₂)₇CF₃) via previously described sol-gel techniques [6-7]. Preparation of the nanocomposites was followed by supercritical processing in a Polaron™ supercritical point dryer to produce aerogel, nanoparticulate materials. Fe₂O₃-SiO₂ oxidizers were subsequently heated at 10 °C/min to 410 °C and held for 4 hours. Following calcination, the oven was switched off and the aerogel oxidizers were allowed to cool to room temperature overnight. Fe₂O₃-SiO_{3/2}-R oxidizers were heat treated under vacuum at 100 °C for 24 hours.

Thermite Preparation

The subsequent energetic nanocomposites were prepared by physically mixing fuel and the aerogel oxidizers. The fuel particles were 80 nm average diameter aluminum (Nanotechnologies Inc.) passivated with an alumina (Al₂O₃) shell that is roughly 4 nm thick and encapsulates the core Al particle. Mixing was accomplished by suspending the relevant amounts of Al and Fe₂O₃-SiO₂ oxidizer in 60 mL of hexane. The mixtures were sonicated using a Misonix Sonicator 3000 sonic wand and the hexane was allowed to evaporate on a hot plate at a temperature of ~80°C. Once the powders were dry, a homogeneous mixture was ready for further experimentation.

Physical Characterization

Transmission electron microscopy (TEM) was performed on a Philips CM300FEG operating at 300 keV using zero loss energy filtering with a Gatan energy-imaging filter (GIF) to remove inelastic scattering. The images were taken under bright field conditions and slightly defocused to increase contrast. The images were also recorded on a 2K × 2K CCD camera attached to the GIF. Energy filtered TEM (EFTEM) element maps were obtained by electron energy loss spectroscopy (EELS) in tandem with the Philips CM300FEG TEM microscope. All EELS measurements were made with a Gatan model 607 electron

energy-loss spectrometer attached to the microscope and were made at the Si-L_{2,3} and Fe- L_{2,3} edges. Images were processed using Digital Micrograph™ 3.3.1 software from Gatan, Inc.

Combustion Velocity Measurements

Combustion velocities were measured using a Phantom IV high-speed camera (*Vision Research*) that records images up to 32,000 frames per second (fps). The camera records visible emission at 128 x 32 pixels and uses a Nikon AF Nikkor 28 mm 1:2.8 D lens. The camera interfaces with a computer that transfers the recorded file from the camera and has a data analysis program from *Vision Research* that measures velocity. For each test, 150 mg of thermite powder mixture was used. Ignition was achieved using a spark ignition system for loose powders in a 0.3175 cm square channel 10 cm in length cut into a transparent acrylic block. All combustion velocities were measured in an open air environment.

DISCUSSION

Synthesis and evaluation of Fe₂O₃-SiO₂-Al energetic nanocomposites

We have previously reported the formulation of Fe₂O₃-Al energetic nanocomposites via an *in situ* sol-gel synthesis of the Fe₂O₃ oxidizing phase that encapsulates aluminum fuel particles [1-2]. The starting materials are simple, inexpensive metal salts, primarily FeCl₃·6H₂O, either nano- or microngrained aluminum particles, and an organic epoxide that initiates Fe-oxide formation through the establishment of a uniform pH gradient in the synthesis solution [8-10]. We have recently expanded this epoxide addition method to the synthesis of Fe₂O₃-SiO₂ nanocomposites containing up to 60 wt% SiO₂. Addition of either TMOS or TEOS to the reaction described above resulted in the first examples of Fe₂O₃-SiO₂ nanocomposites in which Fe₂O₃ is the major component [6]. TEM images of the resulting nanostructures of the aerogel oxidizers are shown in Figure 1 for a Fe₂O₃-SiO₂ oxidizer containing 40 wt% SiO₂. The corre-

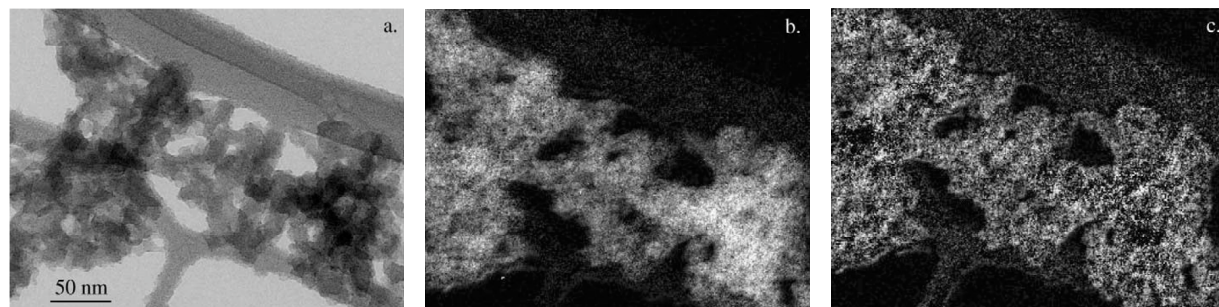
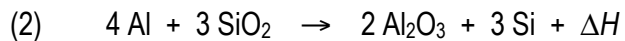
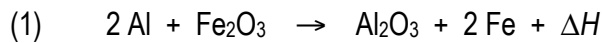


Figure 1. TEM image (a.) of a Fe₂O₃-SiO₂ (40 wt% SiO₂) aerogel oxidizer demonstrating the nanoparticulate structure obtained by sol-gel chemistry. Iron (b.) and silicon (c.) element maps show the dispersion of the Fe₂O₃ and SiO₂ throughout the oxidizer.

sponding Fe and Si element maps show the Fe₂O₃ and SiO₂ components to be mixed on a scale smaller than 5 nm.

The goal of this work is to examine the influence of SiO₂ on the energy release properties of the Fe₂O₃-Al thermite reaction. This objective was accomplished by comparing the combustion velocities of two separate Fe₂O₃-SiO₂-Al nanocomposites: one prepared from mixing commercially obtained nanoparticles of Fe₂O₃, SiO₂, and Al (*Thermite A*); and, the other prepared by combining nanoparticles of Al with the sol-gel prepared, Fe₂O₃-SiO₂ aerogel oxidizers described above (*Thermite B*). In the case of the latter, aerogel powders were chosen due to their superior combustion velocities as demonstrated by Plantier *et. al* [11]. Mixing of the commercial powders with nanometer Al was accomplished using the same method described above (Experimental) for the mixing of the aerogel powders with Al. By studying the two sets of thermites, the effect of sol-gel synthesis on the oxidizer can be isolated with respect to the entire composite.

Six combinations of oxidizers were prepared for *Thermites A and B* ranging from 100% Fe₂O₃ and 0% SiO₂ to 0% Fe₂O₃ and 100% SiO₂ in increments of 20 wt% (*i.e.* 80% Fe₂O₃ and 20% SiO₂, etc). The amount of Al fuel mixed with the two sets of oxidizing phases was calculated according to the amounts needed to produce a complete reaction from chemical equations 1 and 2 based on the molar amounts of



Fe₂O₃ and SiO₂ present in each oxidizer composition. This value was then multiplied by a fuel:oxidizer equivalence ratio (Φ) of 1.2 to obtain the final Al amount. Previous work showed that an Fe₂O₃-Al composite burns at an optimum Φ of 1.2, corresponding to a slightly fuel-rich mixture [11]. The amount of Al fuel metal for each mixture was calculated to vary by no more than 10% over the entire series of thermite nanocomposites.

For this study, characterizing the energetic performance involved measuring the combustion velocity. Flame propagation was examined for loose powders confined on three sides by a channel, but open to an ambient air environment on the top. Although the amount of material and the volume of the channel are controlled, density gradients may still exist along the sample length. Care was taken to ensure homogeneity in the quality of the sample.

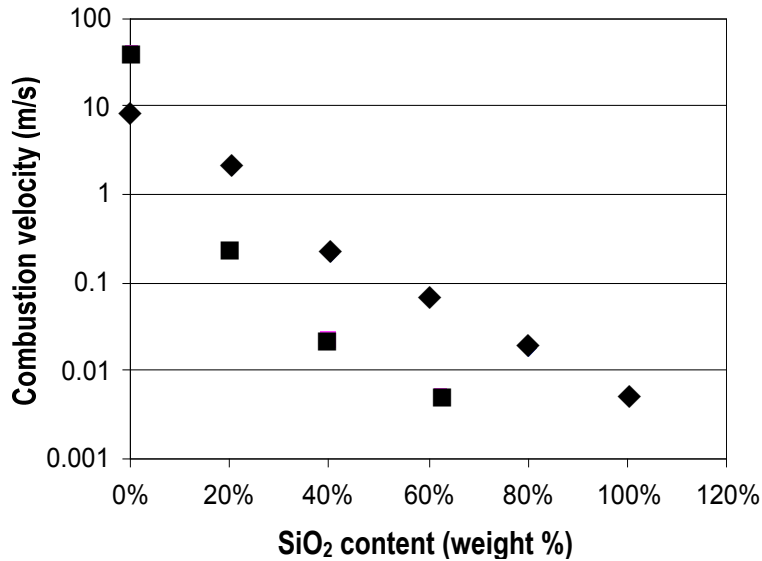


Figure 2. Combustion velocity as a function of SiO₂ content on a logarithmic velocity scale. *Thermite A* (◆) corresponds to the Al combined with discrete nm particles of Fe₂O₃ and SiO₂ and *Thermite B* (■) corresponds to the Al combined with sol-gel synthesized Fe₂O₃-SiO₂ aerogel nanocomposites.

Figure 2 shows the combustion velocity as a function of weight percent SiO₂ content and as a function of the oxidizer synthesis technique. Each data symbol represents an average measurement from 3 or 4 experiments. The standard deviations are ± 0.001 m/s and thus the error bars associated with each data symbol are too small to appear in the plot. For both composites, as the weight percent SiO₂ content increases, the velocity is reduced. This trend is not surprising because the thermal properties of SiO₂ are more insulative than the highly conductive thermal properties of Fe₂O₃. For example, the thermal conductivity for Fe₂O₃ is 20.0 W/m K and for SiO₂ is 1.38 W/m K [12]. The presence of SiO₂ hinders flame propagation by behaving as a thermal heat sink and resisting the transport of heat through the mixture, thereby reducing the velocity. Although SiO₂ contributes to the chemical energy generated, adding SiO₂ reduces the overall speed of the reaction by inhibiting thermal transport and reducing the combustion temperature.

An interesting aspect of Figure 2 is the relationship between the mechanically mixed thermite, *Thermite A*, and the aerogel thermite, *Thermite B*. When no SiO₂ is in the mixture, *Thermite B* produces more than a factor of 4 increase in the velocity over *Thermite A* (*i.e.* 40.5 compared with 8.8 m/s, respectively). The opposite trend, however, is observed for *Thermite A* and *B* when SiO₂ is included in the oxidizer mixture. With 20% SiO₂, *Thermite B* exhibits a 99.4% reduction in combustion velocity, versus only a 76.3% reduction in combustion velocity for *Thermite A*. As more SiO₂ is included, further reductions in

velocity are observed but the difference in velocity between *Thermite A* and *B* remained constant.

Several properties, physical and chemical, may contribute to the different burn behavior of the two sets of thermites. Differences in the chemical properties between the aerogel and commercial Fe_2O_3 appear to exist. In particular, the aerogel prepared oxidizer is comprised of stoichiometric Fe_2O_3 , as characterized by powder X-ray diffraction (not shown). The commercial mixture consisted of amorphous hydrated ferric oxide that possesses bonded water and hydroxyl groups (-OH) within its structure. These chemical impurities have been previously shown to inhibit flame propagation [11].

The major difference between *Thermite A* and *B*, however, may be the result of the different preparation method for the sol-gel produced oxidizers. It has been shown previously that the sol-gel Fe_2O_3 - SiO_2 composite oxidizers prepared for this study consist of nanoparticles which contain both oxide phases in each individual nanoparticle [6-7]. These studies showed no evidence of phase separation between Fe_2O_3 and SiO_2 above 2-5 nm, well below the observed aerogel particle sizes of 10–20 nm (Figure 1). The physically-mixed oxidizers, which are comprised of discrete particles of each oxide component, have Fe_2O_3 and SiO_2 phase separation up to 100 nm, based on the manufacturer's reported particle sizes for the SiO_2 powders. This important distinction is demonstrated in Figure 3. The result of burning *Thermite A* thus causes the particle ejection of the slower reacting SiO_2 from the physically mixed composites, resulting in faster reaction propagation. Reaction propagation for *Thermite A* and *B* containing 40 wt% SiO_2 can be seen in Figure 4. Figure 4a clearly shows discrete particles being ejected from *Thermite A*, however, no such particles are observed in Figure 4b for the slower burning *Thermite B*. In the latter, SiO_2 particles cannot be easily ejected because SiO_2 does not exist as discrete particles (Figure 3), thus the less exothermic $\text{Al} + \text{SiO}_2$ reaction is forced to occur simultaneously with the $\text{Al} + \text{Fe}_2\text{O}_3$ reaction, reducing the

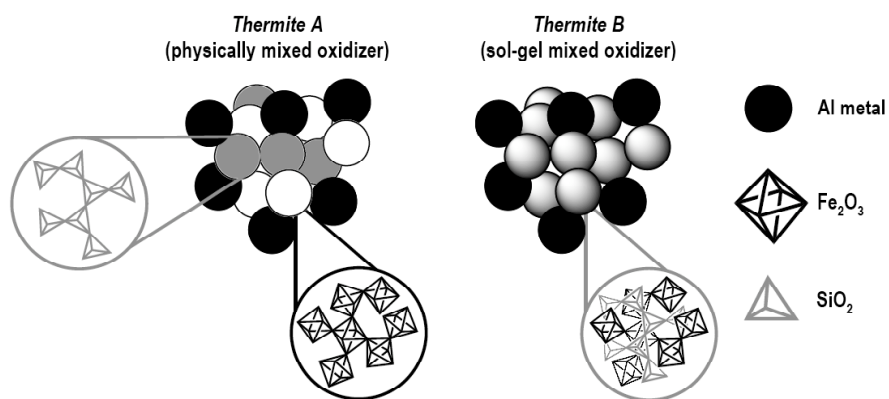


Figure 3. Nanoscale depiction of the different Fe_2O_3 - SiO_2 mixtures in the oxidizing phases of *Thermite A* (commercial, physically mixed powders) and *Thermite B* (sol-gel prepared powders).

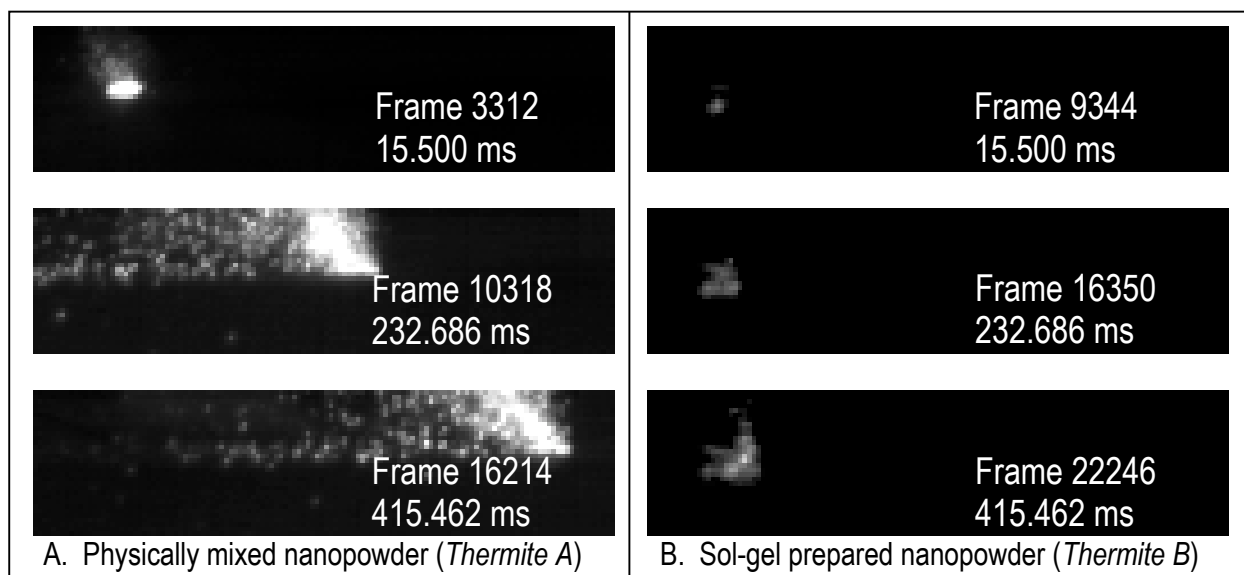


Figure 4. Still frame images from high speed photographic data for A. 40 wt% SiO₂ Thermite A; and, B. 40 wt% SiO₂ Thermite B.

overall burning velocity.

Gas generating Al-Fe₂O₃-SiO_{3/2}-R (R = -(CH₂)₂(CF₂)₇CF₃) nanocomposites.

One limitation inherent in any thermite energetic material is the inability of the energetic material to do pressure/volume-work on an object. Thermites release energy in the form of heat and light, but are unable to move objects. Typically, work can be done by a rapidly produced gas that is released during the energetic reaction. Towards this end, the silica phase of sol-gel prepared oxidizers, in addition to modifying the burning velocities, has also been used to incorporate organic functionality that will decompose and generate gas upon ignition of the energetic composite [3-4,7]. Phenomenological burn observations of these materials indicate that the Al-Fe₂O₃-SiO_{3/2}-R nanocomposites burn very rapidly and violently, essentially to completion, with the generation of significant amounts of gas. Figure 5 shows a comparison of the ignition of an energetic nanocomposite oxidizer mixed with 2 μm aluminum metal without (left) and with (middle) organic functionalization. The still image of the energetic nanocomposite without organic functionalization exhibits rapid ignition and emission of light and heat. The still image of the energetic nanocomposite with organic functionalization also exhibits these characteristics, but it also exhibits hot particle ejection due to the production of gas upon ignition. This reaction is very exothermic and results in the production of very high temperatures, intense light, and pressure from the generation of the gaseous byproducts resulting from the decomposition of the organic moieties.



Figure 5. Still images from the thermal ignition of energetic nanocomposites comprised of sol-gel prepared Fe_2O_3 - $2\mu\text{m}$ Al (left), Fe_2O_3 - $\text{SiO}_{3/2}$ -R- $2\mu\text{m}$ Al (middle), and Fe_2O_3 - $\text{SiO}_{3/2}$ -R-40nm Al (right).

These materials were also mixed with nanometer aluminum. Figure 5 (right) shows a still image of the ignition of the Al- Fe_2O_3 - $\text{SiO}_{3/2}$ -R nanocomposite mixed with 40 nm aluminum. This composite is much more reactive than the same oxidizing phase mixed with 2 μm aluminum metal; the burning of the composite with 40 nm aluminum occurs much too quickly to be able to observe the hot particle ejection. This observation is a good example of the importance mixing and the size scale of the reactants can have on the physical properties of the final energetic composite material. When the degree of mixing is on the nanoscale, the material is observed to react much more quickly, presumably due to the increase in mass transport rates of the reactants, as discussed above.

CONCLUSIONS

We have successfully synthesized energetic nanocomposites using sol-gel methodology. Nanocomposites based on energetic thermites have been produced with both burn rate modifiers and gas generators through a silica-oxidizing phase. The energetic materials display an intimate mixing of all components on the nanoscale. The materials are exothermic when ignited.

These materials have the potential to provide precise amounts of energy and heat at controllable rates. The use of silica burning rate modifiers allows for the control of reaction rate and energy output, two factors that can be controlled based on the method of synthesis and the amount of burn rate modifier present. The ability to precisely control energetic properties also has implications on safety and handling techniques due to the ability to slow reaction rates and decrease the amount of energy released.

Future work will focus on characterization of the products and controlling temperatures and pressures generated by such materials. Such studies will continue to elucidate the influence that

nanoscaled materials will have in the field of energetic composites. These energetic nanocomposites have potential applications as pyrotechnics and propellants.

ACKNOWLEDGEMENTS

This Work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. The authors would like to thank Keith B. Plantier for help with burn velocity determination, and Jennifer S. Harper for TEM and EFTEM analysis.

REFERENCES

- [1] T. M. Tillotson, A. E. Gash, R. L. Simpson, L. W. Hrubesh, J. H. Satcher Jr., J. F. Poco, *J. Non-Cryst. Solids* **285**, 338 (2001).
- [2] A. E. Gash, R. L. Simpson, J. H. Satcher Jr., *Proceedings of the 27th International Pyrotechnics Seminar*, July 15-21, 2001, Grand Junction, CO, U.S.A.
- [3] B. J. Clapsaddle, L. Zhao, A. E. Gash, J. H. Satcher Jr., K. J. Shea, M. L. Pantoya, R. L. Simpson, *Materials Research Society Symposium Proceedings*, **800**, AA2.7 (2004).
- [4] B. J. Clapsaddle, A. E. Gash, J. H. Satcher, R. L. Simpson, *Proceedings of the 31st International Pyrotechnics Seminar*, July 11-16, 2004, Fort Collins, CO, U.S.A.
- [5] A. E. Gash, R. L. Simpson, Y. Babushkin, A. I. Lyamkin, F. Tepper, Y. Biryukov, A. Vorozhtsov, V. Zarko in *"Energetic Materials: Particle Processing and Characterization"*, U. Teipel Ed.; Wiley-VCH, Weinheim, Germany, 2005, pp. 237-292.
- [6] B. J. Clapsaddle, A. E. Gash, J. H. Satcher, R. L. Simpson, *J. Non-Cryst. Solids* **331**, 190 (2003).
- [7] L. Zhao, B. J. Clapsaddle, J. H. Satcher Jr., D. W. Schaeffer, K. J. Shea, *Chem. Mater.* **17**, 1358 (2005).
- [8] A. E. Gash, T. M. Tillotson, J. H. Satcher Jr., J. F. Poco, L. W. Hrubesh, R. L. Simpson, *Chem. Mater.* **13**, 999 (2001).
- [9] A. E. Gash, T. M. Tillotson, J. H. Satcher Jr., L. W. Hrubesh, R. L. Simpson, *J. Non-Cryst. Solids* **285**, 22 (2001).
- [10] A. E. Gash, J. H. Satcher Jr., R. L. Simpson, *Chem. Mater.* **15**, 3268 (2003).

- [11] K. B. Plantier, M. L. Pantoya, A. E. Gash, *Combustion and Flame* **13(7)**, 1-11 (2004).
- [12] R. C. Weast (Editor-in-Chief), *CRC Handbook of Chemistry and Physics 64th Ed.*, CRC Press, Inc, Boca Raton, FL 1984.