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Introduction: Nanoscale Composite Energetic Materials

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ENERGETIC materials are a class of reactive materials containing both fuels and oxidizers. These include propellants, explosives, and pyrotechnics, and are often classified as homogeneous and heterogeneous (composite) materials according to whether the fuel and oxidizer are chemically or physically linked. The use of energetic materials can date to the discovery of black powder in the ninth century. Conventional composite energetic materials are typically composed of particles between 1 and 100 μm. This sets a spatial scale that places a boundary on their maximum reaction rates, and therefore has limited their applications. Homogeneous energetic materials have reactants on the same molecule. Their performance and safety properties, however, are generally not widely tunable. In contrast, nanoscale composite energetic materials may potentially be engineered to improve reliability, control energy release rate, reduce sensitivity, enable multifunctionality, and mitigate hazards. In this publication, a total of 11 papers are included to address various issues of material synthesis, property characterization, reactive processes, and technology implementation in the field of nanoscale composite energetic materials. The purpose is to provide an overview of recent advances in this emerging topical area.

Historically, nanoscale composite energetic materials, or nanoenergetics, have also been termed metastable intermolecular composites (MIC). The field of nanotechnology has struggled to precisely define what is meant by nanoscale. For energetic materials, this scale is typically on the order of 100 nm, or smaller, where significant changes are observed in ignition or reactive properties. Material properties such as melting point may not have changed much at this scale, but the much larger specific surface area can dramatically change the ignition and combustion behavior. For example, a sample of aluminum nanoparticles can be easily ignited in air under room conditions. In contrast, even aluminum powders as small as a few microns are very difficult to ignite in the same environment.

Reaction rates of nanocomposite energetic materials can be increased by several orders of magnitude in comparison with their counterparts at micron scales. This enables many new applications for high-energy reactive composites. A notable example is nanoscale thermites (or superthermites) that have been recently applied to lead-free (or "green") primers and igniters. Nanoscale thermites are much more sensitive and react much faster (higher power) than conventional micron-scale materials, although the energy density of the bulk material is identical. Improvements in performance, such as the burning rate of propellants, can also be realized with the use of nanoscale ingredients.

Synthesis of nanoscale ingredients represents the first step in advancing the technology in this field. Several methods have been developed and implemented commercially, including mechanical alloying (e.g., arrested milling), physical processing (e.g., exploding wire, rapid expansion, and vapor deposition), and chemical processing (e.g., flame synthesis, wet chemistry, and sol-gel). The first paper, by Walter et al. [1], describes recent progress in manufacturing nanoscale aluminum. Some performance data of the nanoscale thermite Al/MoO_3 are also presented.

Many nanoscale materials such as aluminum are passivated with a thin oxide coating. In an oxidizing environment, this coating can grow and thus the material can degrade or age. This issue is addressed in the second paper by Dubois et al. [2], which reports on investigations using coatings to mitigate aging of aluminum and boron powders, and the characterization of these materials. Improved characterization of the performance and physiochemical properties of these materials is needed to develop fundamental understanding of the relationship between the design of engineered nanoscale composites and their properties and performance. The third paper, by Kwok et al. [3], is primarily focused on the characterization of uncoated and coated aluminum nanopowder compositions. Nano-energetic ingredients are characterized using a wide range of techniques to determine the energetic properties, particle morphology, chemical composition, and thermophysical behavior as a function of particle size. The fourth paper, by Johnson et al. [4], focuses on the characterization of powder size distributions using thermogravimetric analysis

The fifth paper, by Schoenitz et al. [5], investigates the ignition kinetics of the nanoscale thermite Al/MoO_3, using scanning calorimetry and heated filament ignition experiments. The chemical kinetics are much more difficult to measure directly because of the presence of condensed phases. Consequently, molecular modeling is beginning to be applied to nanoscale materials. In the sixth paper, Vashishta et al. [6] present their latest results from large-scale atomistic simulations involving chemical reactions of nano-structured energetic materials. The following paper, by Zhao et al. [7], investigates the response of Ni/Al nanolaminates to dynamic loading by means of molecular dynamics methods. Both perfect nanolaminates and specimens with small voids are considered in this nanoscale intermetallic system.

Nanoscale energetic materials can be extremely sensitive to ambient conditions. Therefore, issues such as safety, hazards, storage, and aging must be carefully studied to maximize the full potential of these materials. This can be accomplished by optimizing the particle sizes, morphology, passivating layers, and composition of the energetic material. Sensitivity can be characterized by techniques such as electrostatic discharge (ESD) testing, impact, friction, shock initiation, etc. Some new characterization techniques may also be needed in some cases. In general, laboratory safety is assured by beginning with a small amount of material, using appropriate shielding and personal protective equipment, and characterizing material sensitivity as scaling is performed in incremental steps. The eighth paper, by Puszynski et al. [8], reports studies of the ESD sensitivity of several nanoscale thermites and their ignition and combustion characteristics. The ninth paper, by Sanders et al. [9], reports combustion experiments on four different nanoscale thermites and explains the observations using equilibrium calculations.

Nanoscale composite energetic materials have broad applications for propulsion and energetics. Ultimately, these materials need to be tailored and designed for particular applications. A notable example is microscale actuation and generation of thrust, heat, and power. The tenth paper, by Son et al. [10], examines the combustion of nanoscale thermite Al/MoO_3 in microchannels with dimensions on the scale of 100 μm. Another application is described in the final paper, by Higa [11], on the use of energetic nanocomposites as lead-free electric primers. This application has been extensively implemented, yet many challenges remain.

Many other applications are being considered, and for these to be realized there are many opportunities for future work. Most existing studies have focused on mixed materials. Self-assembly approaches promise much more control over the structured materials. Scaling materials to large amounts is a critical issue that raises many challenges. An important application of this class of materials will also include multipurpose uses, such as reactive structures that can replace inert materials. As discussed in the preceding paragraphs, modeling and simulation in this area remain in their infancy.

Improved models are needed to fully describe the unusual reaction propagation observed. A better, and more comprehensive, understanding of the details of the underlying reactions is needed for these improved models.

New researchers are welcomed to this area, but caution must be exercised to become acquainted with procedures for mitigating the hazards of these materials, which can be very sensitive to unintentional ignition and can react violently. The experimental papers in this special section note some safety practices and issues, but additional detailed and current information is available from those working in the area. Communication with other researchers who are familiar with these materials and appropriate scaling procedures is critically important to avoid incidents.

We wish to express our sincere gratitude to the authors and reviewers for their contributions to this special publication. Their efforts have ensured that the community has an accurate and useful description of the state of the art of nanoscale composite energetic materials as of 2007.

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Steven F. Son
Purdue University

Richard A. Yetter and Vigor Yang
Pennsylvania State University