

Nanotechnology Energetic Material Dynamics Studied with Nanometer Spatial Resolution and Picosecond Temporal Resolution

Dana D. Dlott¹, Hyunung Yu, Shufeng Wang², Yanqiang Yang³, Selezion A. Hambir

Summary

Nanotechnology energetic materials based on size-selected aluminum particles combined with oxidizers can produce twice as much energy as the best molecular explosives and propellants. The fundamental mechanisms of energetic chemical reactions are probed using laser flash heating techniques having picosecond temporal and nanometer spatial resolution.

Introduction

There has been a great deal of interest in nanoenergetic materials recently. These are energetic materials containing at least one nanometric component [1]. Much of the interest stems from the high level of stored energy. It has been known for a long time that the oxidation of metals, particularly aluminum, can generate about twice as much energy per unit volume as the best molecular explosives [1]. For instance Al + nitrocellulose (NC) can generate ~ 16 kJ/cm³ whereas TNT generates only 8 kJ/cm³. But conventional aluminized explosives having 30 μ m average size particles with a wide size distribution have a number of problems, including slow energy release, incomplete combustion, inability to support rapid detonation and so forth. These problems might likely be overcome using nanoparticles, which ought to burn faster and release energy faster. As research on nanoenergetic materials has progressed, several new and exciting ideas have emerged that go quite a bit beyond this straightforward vision of a new powder that promotes faster burning. Developments in nanotechnology indicate that it should be possible to assemble nanoparticles into materials with any desired macroscopic structure. Amazingly, these kinds of materials assembly problems involving control on the nanometer and larger length scales often turn out to be easier than trying to synthesizing new high energy molecules.

¹School of Chemical Sciences, University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

²Present address: Department of Physics, Beijing University, Beijing, P.R. China.

³Present address: Center for Condensed Matter Science and Technology and Department of Applied Physics, Harbin Institute of Technology, P.R.China.

There ought to be some macroscopic arrangement of nanostructures that will do the theoretically best possible job for any specified application. Perhaps optimal solutions will involve some sort of periodic array of fuel nanoparticles passivated with an engineered molecular surface layer having essentially no oxide deadweight, that is linked in controlled ways to oxidizer nanoparticles and organized in layered gradients in three dimensions. Aluminum which is probably the nanoparticle fuels of choice, has not been given much attention by the nanotechnology community, who have done remarkable work with semiconductor and noble metal nanoparticles, so a great deal of work is needed in the materials assembly area. One other area that is absolutely critical for the further advancement of the field of nanoenergetic materials is the development of an understanding of the fundamental mechanisms that underlie material performance, and that is the principal thrust of the research effort in our lab.

Time and space resolved studies of nanoenergetic materials

Nanoenergetic materials consist of at least three parts, a fuel, an oxidizer and an interfacial passivation layer that keeps the fuel from reacting until it is initiated. For Al this passivation layer is normally the native oxide Al_2O_3 , although some research is now looking into tailoring the passivation and depassivation properties using self-assembled molecular monolayers. In this paper, we will describe studies on a simple model system that consists of Al nanoparticles passivated by their native oxide suspended in a polymer matrix that acts as a continuous and uniform oxidizing medium, as shown in Fig. 1. The polymer oxidizer discussed here is nitrocellulose (NC) [2-4], although we have also studied Teflon and nanoparticle oxidizers MoO_3 and CuO_2 .

This paper is focused on two model problems. The first problem is how does a single isolated spherical nanoparticle react with its surroundings. The reactions of a conventional 30-100 μm Al particle with oxidizer, used widely in propellants and explosives, is reasonably well understood in the contexts of mechanical engineering and chemical engineering. Generally the rate of reaction is controlled by diffusive mass transfer between the fuel particle and the oxidizer, and the reaction rate increases proportional to the (particle diameter)^{-1/2}. With nanoparticles, mass and heat transfer processes become minimal, so understanding the nanoparticle problem involves the chemical reaction dynamics of Al + oxidizer reactions as well as diffusive and nondiffusive mass and heat transfer processes on the nanoscale.

In our lab we have developed new methods for studying the nano fuel/oxidizer reactions with high time resolution and high spatial resolution [2-4]. Chemical reactions are initiated by a laser flash-heating pulse. The laser pulse

heats only the skin of the metallic particle since the oxidizer is a transparent dielectric. Whatever else is heated depends on the laser pulse duration and various thermal conduction parameters. In this paper we will concentrate on flash heating pulses of 100 ps duration.

A 100 ps flash-heating pulse is long enough in duration for heat deposited on the skin of the metal nanoparticle to be conducted to the nanoparticle interior so as to uniformly heat the nanoparticle throughout. Not much of the surrounding oxidizer is heated in 100 ps, since NC is an insulator [3]. The metallic component of the nanoparticle is heated to its boiling point and beyond. This is a nearly isochoric heating process, because 100 ps is not enough time for hydrodynamic expansion, so there is a tremendous pressure build up. After a 100 ps pulse, a typical pressure and temperature is 100 GPa and 100,000K. As depicted in Fig. 1, the hot Al atoms originally confined in a sphere of diameter d_{Al} acquire additional energy by reacting with the surrounding oxidizer. On the basis of the chemical stoichiometry, we can determine the thickness d_{sh} of a spherical shell of oxidizer containing just enough material to consume all the Al. The volatile combination of reaction products creates a hot spot in the oxidizer. The hydrodynamic expansion of the hot spot launches a spherical shock wave that expands rapidly in the surrounding oxidizer. As the shock wave expands, its pressure drops. Nitrocellulose is reactive to high pressure shock compression. The NC undergoes shock-induced chemical decomposition. Eventually the pressure and temperature at the shock front is not enough to keep this reaction going. At that instant, the effect of the flash-heating pulse has been the reaction of a sphere of diameter d_{rxn} . This reaction volume is generally larger for larger nanoparticles and higher laser pulse energies.

The second model problem also shown in Fig. 1, is how does the reaction propagate through the nanoenergetic material when there are many interacting nanoparticles. We have simplified this problem as follows [4]. Knowing the diameter and the concentration of nanoparticles, we can compute the average distance between them d_{avg} . Figure 2 shows this calculation for some size-selected nanoparticles used in our lab. The critical parameter is the ratio of the reaction diameter d_{rxn} to the interparticle distance d_{avg} . When $d_{rxn}/d_{avg} \ll 1$, then each nanoparticle is isolated. The individual reaction volumes corresponding to each particle do not reach each other. Only a fraction of the energetic material reacts in this case. However when $d_{rxn}/d_{avg} \approx 1$, the reaction volumes begin to merge as shown in Fig. 1. When this happens the entire energetic material is consumed. By systematically varying the nanoparticle concentration, and then locating the parameter space where the energetic material just becomes totally consumed, we can determine d_{rxn} , the distance of reaction propagation.

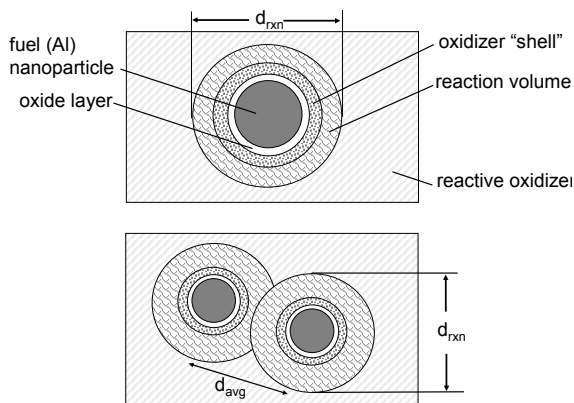


Figure 1. Two model problems. (top) An isolated Al nanoparticle with an oxide passivation layer in a uniform oxidizer, flash-heated by a short laser pulse. The hot metallic fuel reacts with nearby oxidizer in a spherical shell to form a hot spot. The reaction spreads spherically outward from the hot spot to a final diameter d_{rxn} . With many isolated nanoparticles, flash-heating pulse only in spotty oxidizer consumption. (bottom) When the average distance between nanoparticles d_{avg} is equal to d_{rxn} , the reaction volumes merge and the flash-heating pulse results in consumption of the entire nanoenergetic material [4].

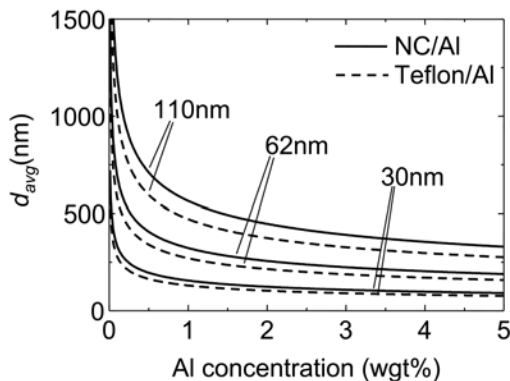


Figure 2. Mean distance between nanoparticles in NC and in Teflon for 30, 62 and 110 nm particles as a function of particle weight fraction. Reproduced from ref. [4], copyright AIP.

Chemical reaction dynamics and the time dependence of reaction propagation are studied by combining laser flash-heating with time-resolved vibrational spectroscopy. The coherent anti-Stokes Raman technique (CARS) is used to monitor the stretching transitions of the ONO_2 (nitrate) groups on the NC

oxidizer [3]. After the Al fuel is flash-heated, it begins to react with these nitrate groups and their characteristic CARS signal begins to disappear. The disappearance occurs in two phases. The first phase represents the reaction between the Al fuel and its NC oxidizer shell. The second phase represents the shock induced chemical reactions spreading through the NC out to a distance d_{rxn} . As shown in Fig. 3, these two phases occur on the ~ 300 ps and 1-5 ns time scales respectively.

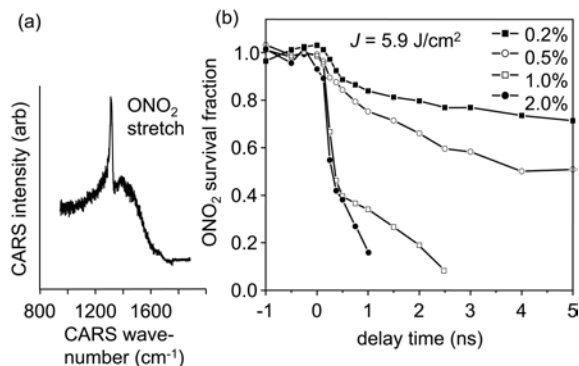


Figure 3. (a) CARS spectrum of NC showing ONO₂ stretch (peak). (b) Time dependence of ONO₂ disappearance in Al/NC with 100 ps flash heating at a fluence $J = 5.9 \text{ J/cm}^2$, shows two distinct phases. The faster ~ 300 ps phase is the reaction between an Al nanoparticle and its oxidizer shell; the slower nanosecond phase is the reaction of the NC oxidizer out to a distance d_{rxn} . Adapted from ref. [3], copyright ACS.

We have conducted extensive studies of the concentration and laser pulse energy dependence of the reaction propagation process using the methodology described above [4]. Some representative results are shown in Fig. 4. The remarkable feature of this plot is that d_{rxn} is a linearly increasing function of the energy E deposited by the flash-heating pulse in the nanoparticle. The way hot spot expansion problems are ordinarily treated is to assume that chemistry is governed by either a critical temperature T_{rxn} or a critical pressure P_{rxn} . As the shock front expands, eventually there is a boundary where T or P drops below the critical value, which determines the outer edge of the reaction volume. The problem with this picture is that T and P are both approximately proportional to the energy density E/V (exact for an ideal gas). For a spherical expansion where E is a constant value and $V \propto (\text{diameter})^3$, the diameter where T and P drop below a particular threshold is proportional to $E^{1/3}$, so in this picture the reaction distance d_{rxn} should not be proportional to E but instead to $E^{1/3}$. We have been able to explain our results using a hydrodynamic model that says chemistry occurs if a critical pressure is applied for a critical time period. In other words the likelihood of chemical reaction is proportional to Pt .

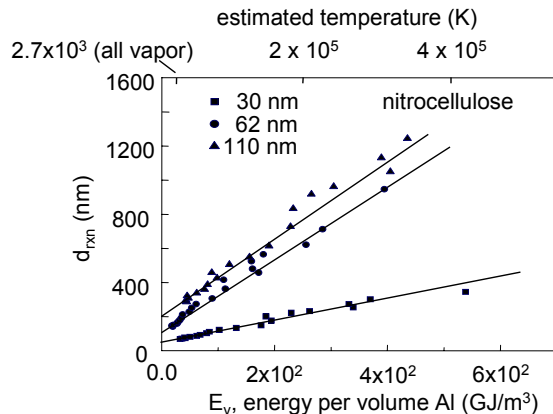


Figure 4. Diameter of shock-induced chemistry volume d_{rxn} in NC vs. E_v , energy per unit volume Al due to flash heating. The estimated temperature T_{est} is given at top. Adapted from ref. [4], copyright AIP.

To summarize: we have developed a model system to understand the reaction of an isolated flash-heated fuel nanoparticle with surrounding oxidizer and the reaction of pairs of interacting nanoparticles a known distance apart. Using laser spectroscopy we can determine how fast a fuel nanoparticle consumes oxidizer with picosecond time resolution. We are also able to determine how far the reaction propagates with nanometer spatial resolution via the merging of reaction volumes.

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Reference

1. L. E. Fried, M. R. Manaa, P. F. Pagoria, and R. L. Simpson, Design and synthesis of energetic materials, *Annu. Rev. Mater. Res.* **31**, 291-321 (2001).
2. S. Wang, Y. Yang, Z. Sun, and D. D. Dlott, Fast spectroscopy of energy release in nanometric explosives, *Chem. Phys. Lett.* **368**, 189-194 (2002).
3. Y. Yang, Z. Sun, S. Wang, and D. D. Dlott, Fast spectroscopy of laser-initiated nanoenergetic materials, *J. Phys. Chem. B* **107**, 4485-4493 (2003).
4. Y. Yang, S. Wang, Z. Sun, and D. D. Dlott, Propagation of shock-induced chemistry in nanoenergetic materials: the first micrometer, *J. Appl. Phys.* **95**, 3667-3676 (2004).