The Advantages and Shortcomings of Using Nano-sized Energetic Materials

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Abstract: Energetic materials are substances that can store chemical energy in their chemical bonds. An ideal energetic material is a substance with high performance, safety and shelf life. Many recent researches have concentrated on the synthesis or the development of new energetic materials with optimized properties, such as thermal stability, sensitivity and burn rate. The reduction of the particle size of energetic materials from micron to nano-sized is one of the suitable approaches for obtaining desirable properties. Recent progress on the reduction of the particle size of energetic materials is reviewed in this work. The effects of nano-sized particles on the performance of energetic compounds are also investigated.

Keywords: energetic compounds, nano-sized particles, sensitivity, burn rate, thermal stability

Introduction

Energetic materials can be classified into three groups *i.e.*, propellants, explosives, and pyrotechnics. Propellants and pyrotechnics release their energy through relatively slow deflagration processes, whilst explosives

can release their energy during fast detonation processes on a microsecond timescale [1].

High performance, safety and shelf life are three important characteristics of an ideal energetic compound. The safety of an energetic material is related to its use without hazards. The safety of energetic materials is defined in terms of the sensitivity of these materials to external stimuli, such as impact, friction and electrostatic discharge. The shelf life of an energetic material is defined as the time between its production and use. An energetic material with high thermal stability usually has a longer shelf life.

In recent years, scientists have tried to improve the properties of energetic material in various ways. Recent progress on the reduction of the particle size of energetic materials is reviewed in this work. The effects of nanosized particles on the performance of energetic compounds are also investigated.

Effects of Nano-Sized Aluminum in Composite Energetic Compounds

The burn rate is one of the most effective factors for propellant performance. The pressure dependence of the propellant burn rate is normally via a power law, which is expressed in accordance with Vieille's law as [2]:

$$r = \alpha P^n$$

where r is the burn rate, α is the burn rate coefficient and n is the pressure exponent. The values of α and n are determined experimentally for a particular propellant formulation, and cannot be theoretically predicted [2].

Nano aluminum powder (nano-Al) has a high thermal conductivity, and is used most widely in the formulation of different propellants. The oxidation of nano-Al is highly exothermic and increases the combustion velocity of propellant formulations [3]. It has been shown that the activation energy for nano-Al oxidation is considerably lower than that for the micron-sized powder [4]. The burn rate can be increased in the compositions of energetic materials containing nano-Al powder [3-8].

A decrease in the activation energy leads to an increase in the reactivity of nano-Al powder because these particles react very fast. Therefore, the ignition and combustion time are reduced as compared to micron-sized Al powder. Nano-Al particles release their equivalent heat in a shorter time than micron-sized Al, and if oxidation of Al particles occurs near the surface of the propellant, the heat

flow released reflects very rapidly towards the surface of the propellants, which can thus increase the burn rate.

Armstrong *et al.* [5] investigated the dependence of Al particle size on the burn rate of a solid propellant at atmospheric (and higher) pressure. They found that a substantial enhancement of the burn rate occurred in the particle diameter range between 200 and 40 nm, as shown in Figure 1. For this range of particle size, the burn rate appears to be asymptotically approaching an inverse particle diameter-squared dependence. This result is true for nano-sized Al because the change in surface area with particle diameter is observed most significantly in the smallest particles. A decrease in the particle size increases the available surface of the particles and the rate of energy release.
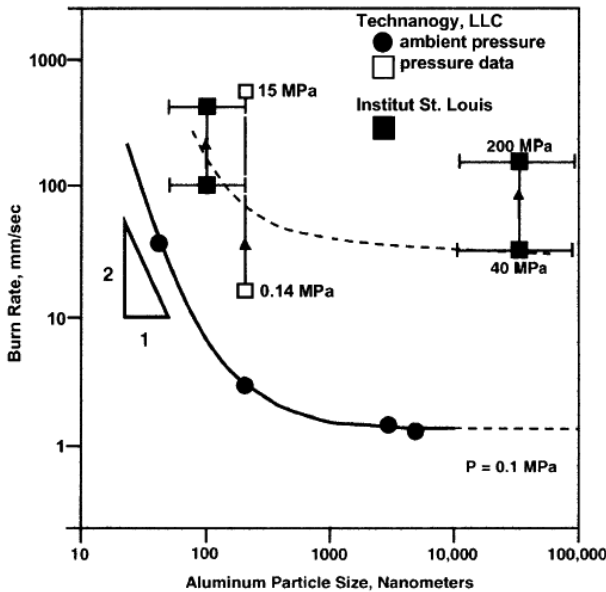

Figure 1. Burn rate as a function of aluminum particle size. Vertical lines show pressure ranges. For constant pressure, there is an inverse square dependence of burn rate on particle diameter at the smallest particle sizes [5].

De Luca *et al.* [6] also studied the effect of the particle size of Al on the burn rate, which is shown in Figure 2. As indicated in Figure 2, the burn rate is essentially not affected by particles in the micrometric range (specific surface area below 1 m^2/g). However, the burn rate is strongly increased by an increase in specific surface area above 10 m^2/g in the nanometric range. Although nano-

sized Al particles enhance burn rates, the shelf life of the compositions with these particles is reduced. De Luca *et al*. [6] reported this observation (see Figure 3).
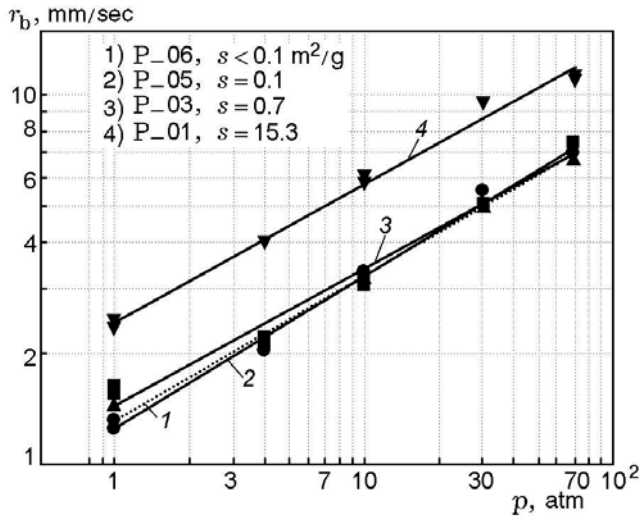

Figure 2.   Increasingly steady burn rates with decreasing specific surface area of aluminum. [6].
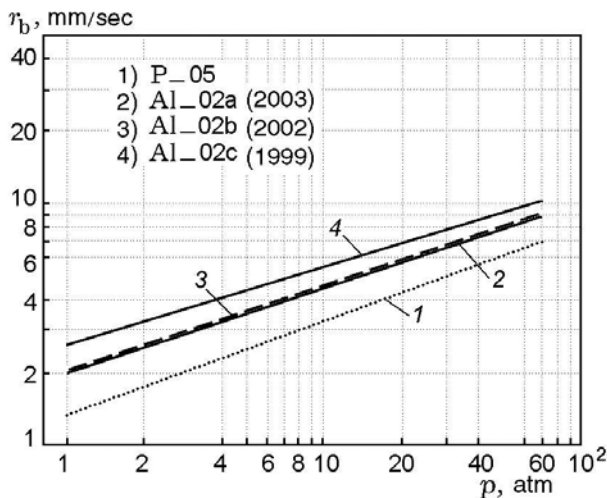

Figure 3.   Increasingly steady burn rates with ageing of nano-Al powder [6].

An aluminum oxide layer protects the core of the Al particles from oxidation. When this layer is exposed to water in air during storage, the Al_2O_3 is converted

into $Al(OH)_3$. Since this conversion leads to a deterioration of the protective surface, the permeability of the structure increases. A result of this process is an undesirable increase in the burn rate which will occur during storage of these propellants. A consequence of this is that the pressure in the combustion chamber will also increase [6, 9].

The sensitivity to external stimuli of compositions such as thermite will be affected by the addition of nano-sized Al. The impact and friction sensitivity of thermite are increased by decreasing the particle size of thermite compositions [10]. When the particle size of a thermite mixture is decreased, its available surface area and reactivity will be increased. Thus, handling and storage of these materials will become more dangerous.

Effects of the Particle Size of Energetic Materials on Their Properties

A knowledge of the sensitivity of energetic materials with respect to unintended initiation is an important safety factor in their use [11-16]. The thermal stability of these materials is an important factor for their shelf life. Nanosizing of explosive crystals can affect their thermal stability. As the explosive's crystal size is decreased from micron to nanometer, the number of crystal defects is reduced. Thus, the probability of hot spot formation due to various external stimuli is reduced, with the possibility of a reduction in the sensitivity to external stimuli. The relationship between crystal defects and hot spot formation has been reported [17]. Nanosizing of explosives leads to a large, available surface area and consequently better heat transmission. However, increased heat transmission reduces the possibility of hot spot formation that can arise from external stimuli.

Yang *et al.* [18] compared the impact sensitivity of nano-NTO with micro NTO. They determined the impact sensitivity (H_{50}) for micro-NTO and nano-NTO as 6.6 J and 8.9 J, respectively. Lee *et al.* [19] also reported that submicron-sized gamma-HMX is less sensitive to friction, impact, and electrostatic discharge, as compared to conventional beta-HMX (see Table 1). Wang *et al.* [20] showed that nano-HNS is less sensitive than micro-HNS to impact and shock stimuli. For the explosive CL-20, it was reported that its sensitivity was decreased by a reduction of the particle size, as shown in Table 1 [21]. Also Li and Brill showed that the impact sensitivity of CL-20 is reduced in energetic nanocomposites [22].

Table 1.   Comparison of sensitivity parameters of explosive materials as a function of their particle sizes

Explosive substance	Crystal size	Impact sensitivity, (J)	Friction sensitivity, (50% load), (N)	Electrostatic sensitivity, (initiation), (J)	Shock wave sensitivity (50% gap thickness), (mm)	Ref.
NTO	micro	6.6	-	-	-	18
NTO	nano	8.9	-	-	-	18
HMX	micro	6.2	116	0.25	-	19
HMX	sub-micro	6.6	156	0.625	-	19
HNS	micro	9.7	-	-	8.05	20
HNS	nano	12.4	-	-	5.10	20
CL-20	15 μ	5.0	64	45	-	21
CL-20	4 μ	6.4	80	49	-	21
CL-20	1 μ	8.0	no reaction	49	-	21
CL-20	0.095 μ	11.0	no reaction	60	-	21
K-6	micro	12.5	64	-	-	23
K-6	nano	15.0	120	-	-	23
RDX	micro	5.8	216	0.25	-	24
RDX	nano*	13.5	216	0.25	-	24
RDX	nano**	18.8	216	0.25	-	24

*Produced by the milling method.
** Produced by the RESS method.

Shokrolahi *et al.* [23] indicated that nano-K-6 (nano-keto RDX) is less sensitive to impact and friction than micro-sized K-6. Render *et al.* [24] showed that nano-RDX has less impact sensitivity as compared to micro-sized RDX, while friction and electrostatic sensitivities for both samples are the same. Song and Li [25] investigated the dependence of particle size and size distribution on the mechanical sensitivity of RDX. They found that impact and friction sensitivities of RDX with a narrow particle size distribution are less than those for RDX with a broad particle size distribution. Their experimental results confirmed that the mechanical sensitivity decreases with a reduction in particle size for both kinds of RDX (see Figure 4).

As mentioned before, thermal stability is another important property of explosives, which can be reflected in shelf life aspects [26-27]. Their safety parameters are increased by improving the thermal stability of these materials. Some studies on the relationship between decreasing particle size of explosives and their thermal stability were reported [26-27]. They confirmed that thermal stability may be reduced by a reduction in the particle size of the explosives.
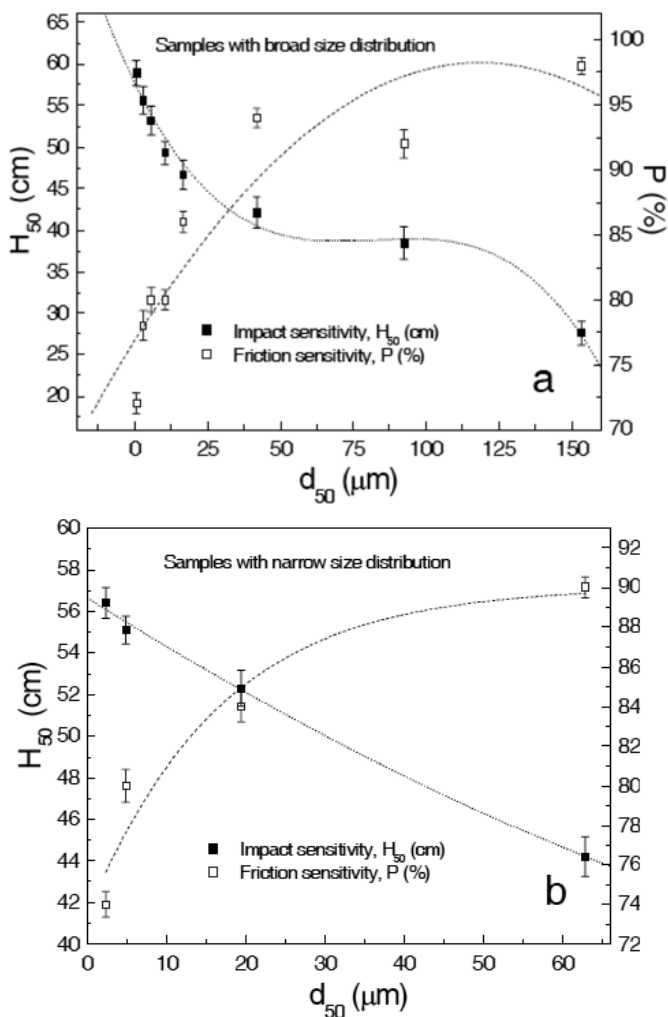
Figure 4. Impact and friction sensitivity of RDX samples as a function of particle size: The error bars are the average and the standard deviation of the average value respectively, obtained from four peering tests. For the impact sensitivity, a weight of 5 kg was used [25].

Since particles with smaller diameters have a higher surface energy, their stabilities are diminished by decreasing the particle size. Thermal stability can be decreased sufficiently to cause a shift in the thermal decomposition peak to lower

temperatures. On the other hand, by decreasing the particle size of explosives, the thermal conductivity is increased. The internal stress is also decreased because of the reduction in lattice defects. This situation was confirmed by Huang *et al.* [28] in their reports on the thermal decomposition of the explosive FOX-7. As shown in Figure 5, the first peak in the DSC curve of FOX-7 is shifted towards higher temperatures by decreasing its particle size. This peak is also barely observed because of the increased thermal conductivity, caused by the decreased particle size of FOX-7. The first peak is related to a nitro-to-nitrite rearrangement in FOX-7, which leads to the destruction of the conjugated system and hydrogen bonds, while the second peak is related to cleavage of the carbon-carbon in FOX-7. The latter is shifted towards lower temperatures by the decreased particle size. The thermal analysis results for micro- and nano-NTO are shown in Figure 6. A shift of approximately 16 °C towards lower temperatures was observed for nano-NTO, as compared to the DSC result for micro-NTO [18].
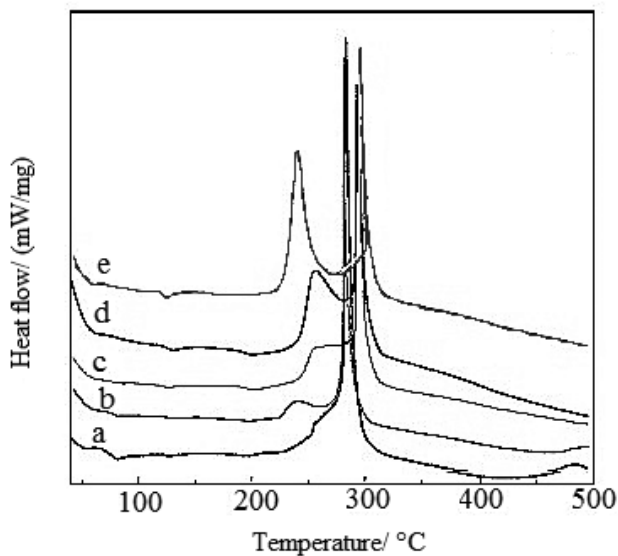

Figure 5.   DSC curves of FOX-7 nanostructures: (a-d) and FOX-7 raw material, (e) between 40 °C and 500 °C at a heating rate of 10 °C /min in N_2 atmosphere [28].
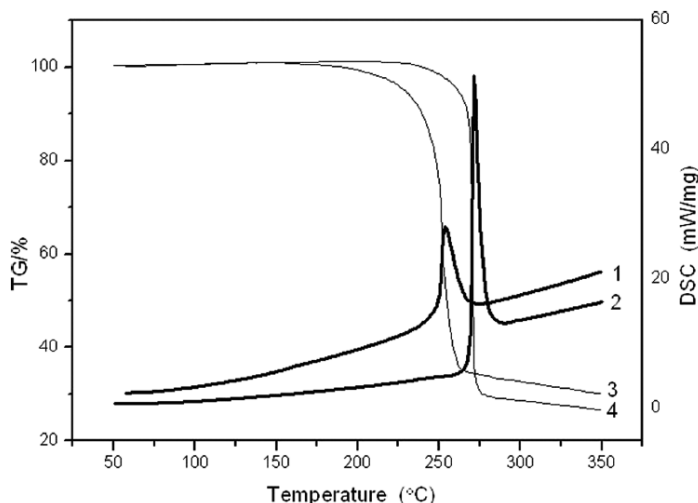
Figure 6. Thermal analysis results for micro-NTO and nano-NTO at a heating rate of 10 °C /min in argon at 2 ml/min. Sample mass 1.5 mg. (1) DSC curve of nano-NTO, (2) DSC curve of micro-NTO, (3) TG curve of nano-NTO, (4) TG curve of micro-NTO [18].

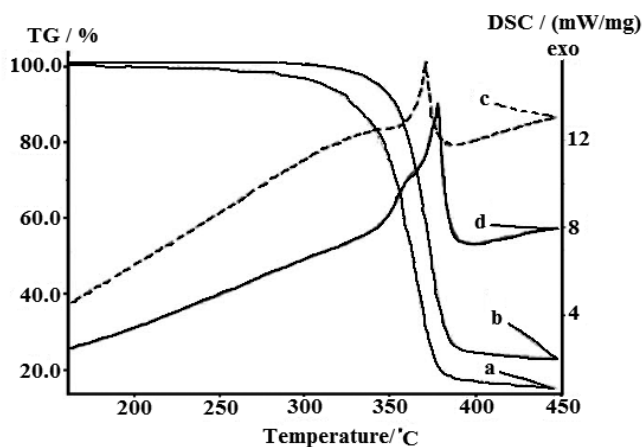**Figure 7.** Thermal analysis results for nano-TATB and micro-TATB at a heating rate of 10 °C/min in argon at 2 ml/min. Sample mass 2.2 mg. (a) TG curve of nano-TATB, (b) TG curve of micro-TATB, (c) DSC curve of nano-TATB, (d) DSC curve of micro-TATB [30].
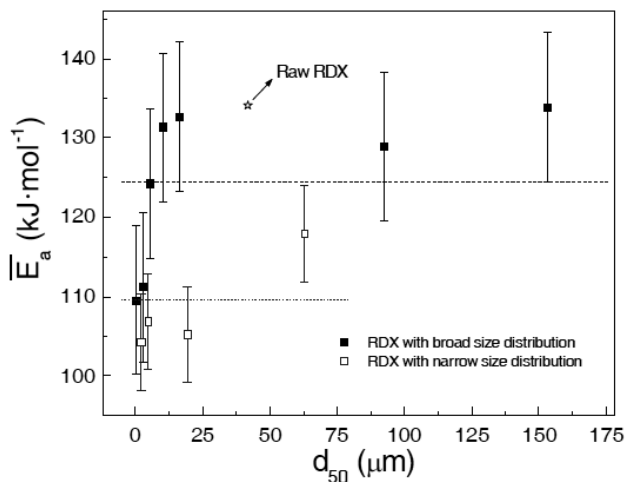
Figure 8.   Plots of $\bar{E}_a$ for RDX against particle size. The error bars are the average and the standard deviation of the average value of $\bar{E}_a$ respectively [25].

Pei *et al.* [29] found that decomposition of nano HMX takes place at approximately 6 °C lower temperature than micro- HMX. Yang *et al.* [30] have shown that there is a shift of approximately 10 °C towards lower temperatures for the exothermic peak of nano-TATB with respect to micro-TATB. Furthermore, TG analysis confirms the fact that nano-TATB has a lower thermal stability than micro-TATB (see Figure 7).

Other research in this area by TG-DSC analyses reveals that the thermal stability of nano-K-6 is lower than that of micro-K-6 [23]. Song *et al.* [25] investigated the dependence of particle size and size distribution on the thermal stability of RDX. As shown in Figure 8, the average value of the activation energy for thermal decomposition of RDX samples with a narrow size distribution is lower than for samples with a broad size distribution.

Wang *et al.* [14] reported that the exothermic peak for the thermal decomposition of nano-HNS occurred at 348.8 °C, whilst for micro-HNS this peak was observed at 349.9 °C. Although both peaks occurred at approximately the same temperature, the heat output of nano-HNS was ΔH=1384J/g whilst for micro-HNS it was ΔH=2124J/g.

Conclusions

Particle size reduction of energetic materials has some advantages and some disadvantages. Nanosizing of the ingredients of propellants leads to an increase in burn rate and in performance. By reducing the particle size of the high explosive constituents of propellants, their sensitivity to external stimuli can be increased. However, this situation leads to a reduced shelf life. Therefore, storage and handling of propellants containing nano energetic materials will be accompanied by hazards. It was found that whilst nanosizing of explosives leads to a reduction in their sensitivity to external stimuli, it often diminishes their thermal stability. When we need to decide whether micrometer particle sized energetic materials should be replaced by nanometer ones, we must to consider this conflict.

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