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PROCESSING, APPLICATION AND CHARACTERIZATION OF (ULTRA)FINE AND NANOMETRIC MATERIALS IN ENERGETIC COMPOSITIONS

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Abstract. The energetic materials research at TNO Defence, Security and Safety, The Netherlands is focusing at the development and characterization of explosives (insensitive munitions), gun/rocket propellants and pyrotechnic compositions and their ingredients. The application of reactive, (ultra)fine and nanometric materials in these compositions has gained increased interest over the past few years. Current research topics focus on the processing, application and characterization of (1) (ultra)fine energetic crystals and composite nano-clusters in plastic bonded explosives, (2) metastable intermolecular composites (MICs) and (3) self-propagating high-temperature synthesis (SHS). In this paper these topics will be highlighted in more detail.

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INTRODUCTION

It is well-known that parameters like mean size, shape, purity and crystallographic structure of solid particles generally affect their physico-chemical properties. From a powder technology viewpoint flowability, dust formation, bulk density, agglomeration, mechanical strength, caking, hygroscopicity, etc. can be mentioned as important parameters which may vary depending on the particle properties. For energetic materials also properties like impact and friction sensitivity, susceptibility towards an electrostatic discharge, decomposition, reactivity towards other chemicals, internal crystal quality (purity, inclusions, defect content), burning rate etc. play an important role. These different properties can be effectively used in order to tailor the processing and/or product properties of the energetic formulations containing these energetic particles. In the more recent past nanosized particles became commercially available and were introduced in energetic formulations, since it was assumed that because of their distinctly different particulate properties as compared to their macroscopic counterparts, they would also lead to significant changes in the properties of the energetic formulations in which they are applied.

This paper provides several examples of the work carried out at TNO Defence, Security and Safety on processing, characterization and application of (ultra)fine and nanometric materials in energetic formulations [1].

EXPERIMENTAL PROCEDURE

(Ultra)fine energetic crystals and composite nanoclusters

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Several co-crystallization methods have been investigated and optimized with the aim to obtain nanocomposite materials consisting of nano-aluminium (n-Al) and the explosive material RDX (cyclotrimethylene trinitramine, $C_3H_6N_6O_6$). For the experiments n-Al from Nanotechnologies Inc. was used, with a mean size of 40.7 nm. The final products were characterized (SEM, thermal analysis, ageing and hazard tests) and one of the co-crystallization methods was successfully scaled up for the preparation of cured, HTPB-based plastic bonded explosives (PBXs), partly containing co-crystallized RDX/n-Al nano-composites with the objective to assess the influence of these nanocomposites on the detonative properties of the PBX. Hereto the PBXs were subjected to shock initiation tests using the Mega Ampere Pulser (MAP) set-up. During this test a flyer plate is accelerated to impact with the PBX sample. The critical flyer velocity v_{critical} is determined at which the sample initiates ('go/no go' level). Details on the MAP set-up can be found elsewhere [2].

Metastable intermolecular compounds

Welding and incendiary mixtures of e.g. fine aluminium powder with a metallic oxide (e.g. Fe_2O_3) – generally referred to as thermites – yield an intense heat when ignited. Thermites are attractive energetic materials because they have a high energy density, show highly exothermic reactions and a high combustion temperature. Nonetheless, the application of thermite materials has been limited because of the relative slow energy release rate compared to other energetic materials. Metastable Intermolecular Composite (MIC) materials are comprised of a mixture of oxidizer and fuel with particle sizes in the nanometer range. One important characteristic of MICs is the fact that the energy release rate can be tailored by varying the size of the ingredients. The nano-scale proximity of the reactants minimizes distances over which the reactants must diffuse in order to react, resulting in dramatically increased rates compared to conventional powder blends. Drawbacks are the sensitivity towards spark ignition and their ageing properties [3-5]. Applications of MICs are e.g. the replacement of Pb-containing igniters [6].

The susceptibility of several MICs and conventional thermites towards an electrostatic discharge has been investigated at TNO by using a specially designed ESD set-up [7]. By including a resistor bank, the spark duration produced by the discharge circuit can be varied from a few μs to ms, since it is known that some materials are more susceptible to initiation by a short, but powerful spark (e.g. explosives), while other materials require a stimulus with a longer duration (e.g. pyrotechnics).

Self-propagating high temperature synthesis

Self-propagating high-temperature synthesis (SHS), also known as solid-flame combustion or combustion synthesis, is a gasless combustion process. SHS is a cost-effective method for producing high-purity refractory compounds and advanced ceramics, including functionally gradient composite materials [8]. The basis of the reaction synthesis relies on the ability of gasless and highly exothermic reactions to be self-sustaining.

SHS has assumed significance for the production of intermetallics, ceramics and cermets, because it is a very rapid processing technique which avoids complex furnaces [9]. One of its drawbacks is the high porosity of the final product (typically 50% of the Theoretical Maximum Density). Therefore, a subsequent densification step is required, though this is often hard to achieve in ceramic composite materials, because they are highly deformation-resistant. However, when the reaction product is still hot, one may take advantage of its ductile behaviour and apply techniques as hot (quasi-isostatic) pressing, hot rolling or shock waves to eliminate or reduce porosity.

Powder metallurgical arcing contact materials are composite materials used in medium and high current applications such as circuit breakers and switchgears [10]. The homogeneity of their micro-structure is essential for the physical characteristics and the switching performance of the electrical contacts. The main requirements for an arcing contact electrical material include high electrical conductivity, elevated melting point and high hardness. Recently TiB_2-based cermets in a Cu or

Al metallic phase for electrical contact applications have been successfully produced via SHS and quasi-isostatic pressing (QIP) at TNO [11]. As starting materials high-purity (99.9%) powders of amorphous B (1 μm), Ti (45 μm), Cu (63 μm) and Al powder (1.2 μm) have been used in the tests.

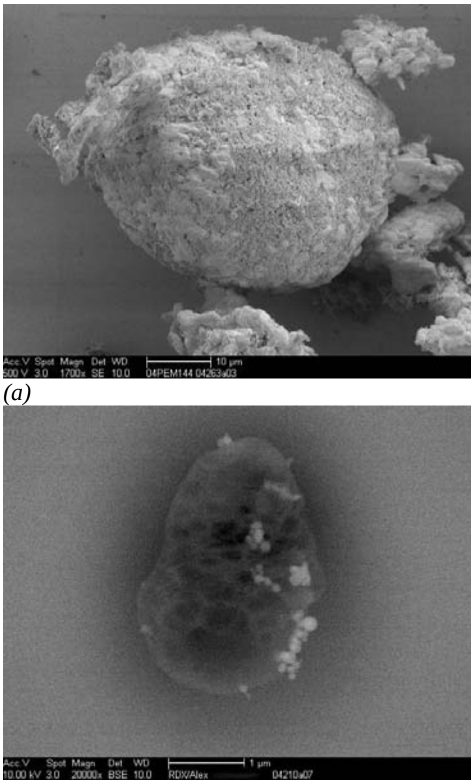
RESULTS AND DISCUSSION

(Ultra)fine energetic crystals and composite nanoclusters

Several examples of co-crystallized RDX/n-Al composites are shown in Fig. 1. Generally, the size of the more or less rounded particles ranged from several tens of microns to submicron [1]. The coating of the n-Al with RDX was not ideal, although at least a part of the n-Al particles appeared to be covered by RDX, as was shown by X-ray micro-analysis, taken from the centre of the largest RDX/n-Al composite shown in Fig. 1(a). This clearly shows that Al is present, next to C, N and O resulting from RDX. As no n-Al particles or clusters can be observed at the surface of this RDX particle – contrary to Fig. 1(b) – it is concluded that the n-Al is inside the RDX crystal.

The impact and friction sensitivity data shows that RDX mixed with n-Al (40.7 nm) is more friction sensitive than the same RDX mixed with 6 μm Al (80 vs. 160 N). The co-crystallized RDX/n-Al is even more sensitive (60 N). Probably this is related to a more intimate contact between the RDX and n-Al particles in the co-crystallized sample compared to the physical blends. Clearly, the presence of (n-)Al sensitizes the RDX, since a blank measurement (no Al present) yields a friction sensitivity of 240 N. A re-crystallized RDX sample without (n-)Al showed the lowest sensitivity towards a frictional stimulus (360 N). For all samples tested, the impact sensitivity did not change (all 7.5 Nm).

Thermal analysis tests (TG/DTA, DSC) were performed in order to assess differences in reactivity and decomposition characteristics of RDX/n-Al compositions. The results obtained with co-crystallized RDX/n-Al and a physical blend of recrystallized RDX and n-Al indicated a lowering of the melting and decomposition temperatures of RDX compared to what is generally found for (coarse) RDX. The results indicate that the recrystallized RDX consists of a range of particle sizes, the smaller ones revealing properties similar to nanometric RDX and the larger ones showing features of 'standard' RDX. The lower melting and decomposition temperatures of nanometric RDX can be attributed to the fact that as a result of the high surface area of the nanometric particles (large surface to volume ratio), the bulk properties become governed by surface properties. This is substantiated by other literature data [12] and quantum mechanical calculations [13].



(a)

(b)

Figure 1. Examples of co-crystallized RDX/n-Al composites. In (b) n-Al particles are attached to an RDX particle.

Plastic bonded explosives (PBXs) were prepared according to the compositions shown in Table 1. In order to prevent problems with PBX processing (increased viscosities when using small particles), the fine particle content was limited to ~18 wt%. The results of the shock initiation (MAP) tests are

Table 1. PBX batches prepared on 250 g scale (contents in wt%). Solid load is 76.0 wt% for all formulations.

PBX	Coarse RDX	Fine RDX incl. n-Al [a]	Fine RDX	n-Al [a]	Al (6 μm)	HTPB
RU-172	57.9	–	14.5	–	3.6	24.0
RU-173	57.9	–	14.5	3.6	–	24.0
RU-174	57.9	18.1 (co-cryst. with n-Al)	–	–	–	24.0

[a] n-Al from Technanogy, mean size 40.7 nm, Al_2O_3 content 56.6 wt%.

listed in Table 2. The PBX containing conventional Al (6 μm) is less shock sensitive than the PBXs containing n-Al (higher v_{critical}). No difference was observed between the PBX with co-crystallized RDX/n-Al and the physical blend of RDX and n-Al. The detonation velocity is the same for all three PBXs. The difference between the reference and the n-Al containing PBXs may well be related to the difference in the overall active Al content in the 6 μm Al (~99 wt%) and the n-Al (56.6 wt%). However, it is practically impossible to replace Al with n-Al while keeping all other properties constant (solid load, RDX content, active Al content, etc.).

Table 2. Shock initiation results of three PBX formulations by flyer impact (125 μm kapton); v_{critical} = critical flyer impact velocity; V_{det} = measured detonation velocity.

PBX	v_{critical}, km/s	V_{det}, km/s
RU-172	3.7 ± 0.2	7.3 ± 0.2
RU-173	3.1 ± 0.2	7.3 ± 0.2
RU-174	3.1 ± 0.2	7.2 ± 0.2

Thermodynamic calculations using a kinetic module in Cheetah 2.0, on composition PBXN109, have addressed the influence of Al reaction rates on V_{det}, detonation pressure (p_{det}) and temperature [14]. Although a high Al reaction rate leads to a fast heat release, V_{det} and p_{det} may be negatively influenced because of the fact that the reaction of Al mainly yields solid reaction products (Al_2O_3), thereby taking away oxygen from the gaseous detonation products. This may therefore explain some of the results of (other) Al-containing PBXs in which conventional Al has been replaced by n-Al.

Metastable intermolecular compounds

Table 3 shows the threshold ESD energies, i.e. the minimum energy for the ignition of indicated samples. The value $\frac{1}{2}CV^2$ is the energy stored on the capacitor. When possible the value of E_{spark}, the energy deposited in the spark through the sample, is given as well. With no series resistance in the discharge circuit, short duration pulses of the order of μs are created. With a 10 kΩ resistance, the pulse duration will be on the order of 0.1-1 ms, depending on the capacitor value.

The order of ESD sensitivities is more or less the same looking either at the capacitor energy in a short and long duration pulse, or at E_{spark}. Samples #1, #4 and #6 are the most sensitive, and #7 is the least sensitive. Actually #6 is so sensitive that the reproducibility in sensitivity threshold is difficult to measure and/or the ESD equipment has difficulty in reproducibly generating a low E_{spark}.

The ESD sensitivity depends on the mean size of the reactants used. This is evident by comparing samples #7 and #8, containing Al and n-Al respectively, and previous measurements presented on various mixtures of n-Al and (n-)MoO_3 [7]. Sample #4, though consisting of micronsized particles of Al and Bi_2O_3, is rather spark sensitive, indicating that a nano-version of this composition might initiate even more easily.

Samples #1 and #2 have the same stoichiometry of n-Al and n-Fe_2O_3, but use a slightly different mean particle size of Al. Assuming that reactivity increases with decreasing particle size, sample #2 was expected to be more sensitive than #1, but the opposite is observed. This may well be related to the higher Al_2O_3 content of the n-Al used in #2.

Another interesting phenomenon is the influence of sample stoichiometry on ESD sensitivity: the stoichiometric mixture of B and Ti (sample #6) is more reactive than the non-stoichiometric one (#5).

MICs can also be rather impact and friction sensitive, as is illustrated by the following examples: the impact sensitivity of a mixture containing n-Al, MoO_3, NC and IDP (65.0/24.4/5.3/5.3 wt%) was > 50 Nm, whereas for composition with n-Al, n-MoO_3 and VitonA (65.0/24.4/10.6 wt%) this was 4 Nm; the friction sensitivity in both cases was found to be < 5 N. These hazard properties show that MICs can be extremely sensitive towards impact, friction and spark, and should be handled only if proper safety measures have been applied.

Table 3. ESD sensitivities of several MICs compared to conventional thermites.

Sample	Sample ingredients	Specifications	Resistance, kΩ	1/2 CV^2 (E_{spark} [a]), J
#1	2 n-Al + n-Fe_2O_3	n-Al 100 nm (Al_2O_3 content 31.9 wt%);	0	0.026
		n-Fe_2O_3 90 nm	10	1.8
#2	2 n-Al + n-Fe_2O_3	n-Al 40.7 nm (Al_2O_3 content 56.6 wt%);	0	0.29 ($3.4 \cdot 10^{-3}$)
		n-Fe_2O_3 90 nm	10	4.4
#3	C + Ti	C, Ti < 10 μm	0	0.40 ($1.3 \cdot 10^{-3}$)
			10	16.8
#4	2 Al + Bi_2O_3	Al < 10 μm; Bi_2O_3 < 6 μm	0	0.051 (~ $2 \cdot 10^{-3}$)
			10	0.50
#5	B + Ti	B < 1 μm; Ti < 10 μm; (non-stoichiometric ratio)	0	0.40 ($2.3 \cdot 10^{-3}$)
			10	6.4
#6	2 B + Ti	B < 1 μm; Ti < 10 μm (stoichiometric ratio)	0	0.13 ($0.6 \cdot 10^{-3}$)
			10	0.01
#7	2 Al + Ti	Al, Ti < 10 μm	0	1.3 ($13.8 \cdot 10^{-3}$)
			10	no initiation
#8	2 n-Al + Ti	n-Al 40.7 nm (Al_2O_3 content 56.6 wt%);	0	0.58 ($6.2 \cdot 10^{-3}$)
		Ti < 10 μm	10	16.8

[a] True spark energy is measured from the voltage and current through the sample. At the moment sensors permit reliable measurements only at spark energies above ~ 1 mJ and at relatively short duration pulses (so only at 0 kΩ).

A potential application of MICs is as energetic fragments which ignite upon impact with a target [15]. Currently tests are planned with pressed MIC and conventional thermite samples (selected from table 3) fired onto a target with a 30 mm caliber canon, as well as experiments to determine the deformation sensitivity of the MICs using a so-called ballistic impact chamber (BIC) test set-up [16], which has recently been constructed at TNO.

Self-propagating high temperature synthesis

SHS experiments have been carried out with TiB_2 in an Al and Cu metallic phase. The relative densities of the TiB_2-Al cermets are high (max. 98% of the theoretical mean density, TMD), but those of the Cu-based cermets are too low (57-67% TMD). Numerical simulations with ABAQUS have been performed, modelling the cooling of the TiB_2 cermet after the SHS reaction in order to optimize the QIP conditions for reaching higher densities of the TiB_2-Cu cermets. The simulations show that the Cu-based cermet cools down sufficiently slowly, allowing an extension of the time-window during which the load is applied with the objective to increase the density by squeezing molten Cu into the open pores in the ceramic phase without cracking or breaking the ceramic [17].

In the near future the focus of this research will shift to the kinetics of an SHS reaction, i.e. assessment of the combustion velocity as a function of particle size and reactants ratio.

CONCLUSIONS

This paper illustrates that the availability of (ultra)fine and nanomaterials provides new tools to tailor the properties of energetic formulations. Their use, however, may also introduce drawbacks, such as an increased susceptibility to impact, friction and spark, requiring adequate safety measures. Another disadvantage is related to potential difficulties in the processing of castable compositions like PBXs and solid composite propellants when introducing nanomaterials, since these will increase the viscosity of the mixture. This should be able to be circumvented by using an extrusion rather than a casting technique. Furthermore, the combination of experiments and numerical modelling using dedicated software tools, has proven to be a successful approach in developing a better understanding of the phenomena playing a role when including (ultra)fine and/or nanomaterials in energetic formulations. Obviously, the application of nano-materials is not limited to the energetic formulations discussed in this paper, but may also comprise rocket and gun propellants. TNO is involved in these developments as well.

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