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Review / Przegląd

Mixtures of nanometric thermites and secondary explosives versus primary explosives *Mieszanki nanometrycznych termitów i materiałów wybuchowych kruszących a materiały wybuchowe inicjujące*

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Abstract: Possible substitutes for primary explosives containing lead may be compositions of the NSTEX type – mixtures of nanostructured thermites and explosives. These compositions, exhibit a number of unconventional features, intermediate between primary explosives and secondary explosives. These properties, make them the promising substitutes for primary explosives containing heavy metals, such as lead. The aim of this paper, is to identify the potential of application, possible challenges and risks associated with this issue.

Streszczenie: Ewentualnym zamiennikiem materiałów wybuchowych inicjujących zawierających ołów mogą być kompozycje typu NSTEX – mieszaniny nanometrycznych termitów i materiałów wybuchowych. Kompozycje te wykazują szereg niekonwencjonalnych cech, pośrednich pomiędzy materiałami wybuchowymi inicjującymi a materiałami wybuchowymi kruszącymi. Właściwości te czynią je obiecującymi zamiennikami materiałów wybuchowych inicjujących, zawierających metale ciężkie, takie jak ołów. Celem pracy, jest określenie potencjału zastosowania, możliwych wyzwań i zagrożeń związanych z tym zagadnieniem.

Keywords: MIC, NSTEX, DDT

Słowa kluczowe: MIC, NSTEX, DDT

Symbols and abbreviations

AN	ammonium nitrate(V), NH ₄ NO ₃
CL-20	2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaasa-isowurtzite
D	detonation velocity [m/s]
DDT	deflagration to detonation transition
DSC	differential scanning calorimetry
D-RDX	fine-grained RDX

FPV	front propagation velocity [m/s]
G-RDX	coarse-grained RDX
HTPB	hydroxyl-terminated polybutadiene
HE	high explosive
MIC	metastable intermolecular composites
MDM	melt dispersion mechanism
MWCNT	multi-walled carbon nanotubes
EM	explosive material
IEM	initiating explosive material
NSTEX	nanostructured thermites and explosives
PETN	pentaerythritol tetranitrate, pentrite
RDX	1,3,5-trinitro-1,3,5-triazacyclohexane
t	time [s]
T	temperature [K]
TMD	theoretical maximum density [g/cm ³]
TNT	2-methyl-1,3,5-trinitrobenzene, TNT
$T_{top,p}$	fuel melting point [K]
$T_{top,u}$	oxidant melting point [K]
SDT	shock to detonation transition
Γ_K	relationship between the Tamman temperature characteristic of the oxidant and the melting point of the fuel [K]

1. Introduction

Lead salts such as lead(II) azide and lead(II) 2,4,6-trinitrobenzo-1,3-diolate are common primary explosives used in initiation systems in civilian and military applications [1]. Their use is determined by their detonation parameters and the extremely short induction times of the high-energy transition [2]. However, these compounds and their production processes are dangerous, both for personnel and the environment, which is primarily due to their high sensitivity to mechanical stimuli [3] and the harmful effects of lead compounds on the environment. This results in the need to develop new, more environmentally friendly primary explosives. Among the compounds developed to date, mention can be made of, among others:

- chlorate(VII) μ -4-amino-1,2,4-triazol- μ -dichlorocopper(II) [4],
- nickel hydrazine nitrate [5],
- 4,5-bis(dinitromethyl)-3,3'-furoxan potassium [6],
- 4,4'-bis-(dinitromethyl)-3,3'-azofuraxane [7],
- 4,8-dinitroaminodifuraxane[3,4-b,e] pyrazine [8].

Among the properties initiating explosives must exhibit, authors [9, 10] point to:

- high initiation capacity,
- a range of sensitivity to external stimuli to ensure safe working while allowing stimulation of high-energy transition with a low-energy stimulus,
- chemical stability over a wide temperature range,
- compatibility with construction materials and HEs,
- short time and distance to develop a stable detonation.

These varying requirements for initiating explosives make the development and engineering of environmentally friendly, lead-free primary explosives a major concern.

Nanothermites and the NSTEX compositions derived from them form a promising group of high-energy compositions containing mainly aluminium as the fuel. Numerous characterisation studies of these compositions have been carried out in recent years. The properties of the compounds in this group have led to an increase in research aimed at developing products using these compositions. Despite obstacles such as

high price, complex production processes, quality requirements for the raw materials used, the share of the above group in applications involving initiation systems is expected to increase. This paper aims to discuss the background information on these compositions, the mechanism of their transition and to identify the potential for substitution of lead compounds in the role of dominant IEMs.

2. Nanothermites and NSTEX compositions

Nanothermites, also referred to as superthermites or MICs, usually consist of a metallic fuel and a metal oxide or salt as an oxidant, where at least one of the components is characterised by nanometric fragmentation [11]. The most common fuels used in these mixtures include aluminium, boron, silicon, magnesium, tantalum and titanium [12]. Copper(II) oxide, iron(III) oxide, molybdenum(VI) oxide, bismuth(III) oxide, tungsten(VI) oxide, sulphate(VI), iodate(V) and iodate(VII) salts are among the most commonly used oxidants [12]. For nanomaterials, a drastic improvement in heat and mass transfer conditions is observed with respect to thermite compositions, whose components are characterised by micrometric fragmentation. Consequently, this group of high-energy materials exhibits a number of interesting properties, including [12, 13]:

- ignition at lower temperatures than an analogous composition with micrometric fragmentation of the components,
- increased sensitivity to initiating stimuli than an analogous composition with micrometric fragmentation of ingredients,
- higher linear burning rates, typically in the range of 100-1000 m/s, but values in the order of 2500 m/s are indicated in papers [14, 15],
- characterised by low induction times and the development of a stable combustion process.

Currently, there is no consensus on an accurate, complete and verified mechanism for the combustion process of nanothermite compositions. Most often, it is emphasised that the combustion processes of nanothermites occur according to a convection mechanism [16], where a high degree of homogenisation of the composition and a small particle size allow the assumption that the combustion processes are limited only by the reaction kinetics [12, 16] and that the influence of diffusion is limited. At the same time, it is assumed that for particle sizes of 40-200 nm it is acceptable to adopt a continuous medium model and to use classical thermodynamics to describe and simulate nanothermite combustion processes. Specific models to explain the reaction mechanism of nanothermites are the MDM mechanism and the reaction sintering mechanism. However, it should be emphasised that the mechanisms outlined below are described in the paper in a general way in order to highlight the most important properties of these models.

The MDM mechanism has been proposed in paper [17], for compositions containing nanometric aluminium. The authors of the paper assume that the rate of pressure and temperature build-up at the reaction front is too fast for combustion to be controlled by diffusion of oxygen through the oxide layer covering the fuel surfaces. Based on paper [18], the authors concluded that, if the rate of temperature increase is greater than 10^6 K/s, rapid core melting of aluminium grains covered by an oxide layer occurs, where the core phase change occurs before the oxide layer is unsealed. The decrease in density of the core (by 8.78%) caused by its melting generates an increase in the pressure acting on the oxide layer in the order of 0.1-4 GPa. This rapid increase in pressure leads to a sudden rupture of the oxide layer and the atomisation of aluminium “droplets” in the medium at velocities in the order of 100-250 m/s, during which oxidation takes place.

As a critical parameter, which determines the possibility of the burning process occurring according to the above mechanism, the authors of paper [19] indicate the Tamman temperature of the metal oxide used as an oxidant and its ratio to the melting point of the fuel, in accordance with Equations 1 and 2.

$$T_{\text{Tamman}} = \frac{T_{\text{top},u}}{2} \quad (1)$$

$$\Gamma_K = \frac{T_{\text{Tamman}}}{T_{\text{top},p}} \quad (2)$$

This parameter allows an estimation of the effect of temperature increase on the mechanical properties of the oxide layer and determines the ability of the melting grain core to be “held” by the tight oxide film. In paper [19] the authors predict, on the basis of calculations, that an MDM mechanism is possible for compositions containing Al, Ca, Mg, Yb, Zn, Li as fuel. In papers [17, 19], the authors point to the following as parameters determining the possibility of this mechanism occurring and affecting it:

- existence and properties of the passive layer,
- the temperature at which the oxide film forms, which determines the initial stresses in the molecule and core,
- fuel core porosity,
- ratio of oxide layer thickness to core diameter,
- defects in the oxide coating,
- particle size distribution,
- centre heating rate.

In papers [20, 21] the authors discussed the mechanism of reactive sintering. The heterogeneous reaction between fuel and oxidant is initiated at the interfacial surface. The heat generated by the exothermic reaction at this surface is conducted deep into the material and is transferred through the gaseous intermediate products of the reaction. If the amount of heat supplied from the reaction front is sufficient to melt the components in the zone adjacent to the reaction zone, surface tension and capillary forces drive the rapid movement of the liquid material to the surface interface where the reaction takes place. Below the melting point of the components, mass transport can be driven by diffusion at grain boundaries in the solid phase. However, an increase in reaction rate above the melting point of any of the compositional components indicates a key contribution from heterogeneous reactions [21]. However, it should be borne in mind that oxidation of the fuel by intermediate gaseous reaction products in the zone of their migration is possible, occurring simultaneously with the reaction at the combustion front.

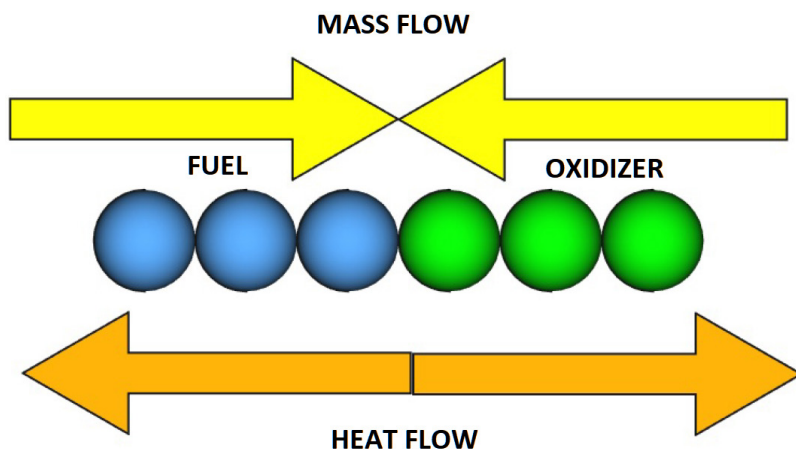


Figure 1. Schematic diagram of the reaction sintering process (based on [21])

Based on experiments and calculations, the authors of paper [20] have shown that if the reaction temperature is sufficient to melt one of the components, the time of the sintering process follows the reaction time, indicating that the combustion process is directly limited, precisely by the sintering process. An important conclusion from this mechanism is that there is no effect of reducing particle fragmentation below a certain limit value on improving high-energy parameters [16, 22].

It should be noted that high-energy nanothermite transitions, despite the often occurring supersonic velocity pressure wave [14, 23], cannot be classified as a detonation process. This is confirmed by the decrease in

burning rate of nanothermites with increasing density and thus decreasing porosity [14, 23, 24], the small amount of gaseous products generated, the wave front overpressure low compared to typical EM [15, 25] – not strong enough to initiate and sustain detonation, and the relatively slow pressure build-up rate with respect to the detonation regime [26-28].

Potential applications for this group of high-energy materials include igniters, detonators, primers, correction motors, decontamination devices, current protections, delay systems, gas generators [11, 12, 25, 29]. It is also possible to use the aforementioned compositions as additives for rocket fuels, gun propellants and HEs. Hybrid compositions, most commonly referred to as NSTEX compositions, are usually defined as a mixture of nanothermite and another high-energy material, typically an HE. Many authors point to the possibility of using NSTEX-type compositions as possible “green” substitutes for lead salts [11, 12, 19] in the design of initiating agents. Compositions of this type show intermediate properties for both groups of materials used in their preparation. They are typically capable of stable detonation through a DDT-type transition [30], while also achieving maximum explosive performance faster than HEs [31]. The sensitivity to initiation stimuli of NSTEX compositions relative to pure high-energy materials depends on a number of factors. Most commonly, NSTEX-type compositions exhibit lower friction sensitivity than pure HEs, but increased impact sensitivity [29, 31]. An overview of the factors influencing sensitivity to initiating stimuli is presented using the Al/Fe₂O₃/RDX composition as an example [32]. The sensitivity to electrical spark and laser radiation is closely related to the composition [33]. The detonation velocities of these systems are lower than those of the pure HE and are dependent on the proportion of nanothermite in the composition. The authors of paper [30] observed this relationship for compositions consisting of hexogen with the addition of nanothermite Al/WO₃. The velocity of the high-energy transition, depending on the mass ratio Al/WO₃:RDX, is in the range 2000-3500 m/s. The ratio of nanothermite to HE is one of the main parameters which determines the mechanism of the high-energy process. Compared to pure HE, NSTEX compositions show up to two to four times higher heat of explosion [34].

Compositions based on gun propellants and rocket fuels with the addition of nanothermites, are also classified as NSTEX. They exhibit increased burning rates, higher combustion heats and have a faster pressure build-up relative to high-energy materials without the addition of nanothermite. For example, in paper [29], the authors studied the effect of the addition of nanothermite Al/Na₂SO₄ on the improvement of the high-energy performance and on the combustion mechanism of Vectan A1 gun propellant. Paper [35] demonstrated an increase in the burning rate of solid heterogeneous rocket fuel based on ammonium chlorate(VII) (NH₄ClO₄), aluminium dust and HTPB.

3. DDT process

The range of possible system conditions and initiating stimuli which can lead to DDT is extremely wide. DDT may occur in high-energy materials, gas-air mixtures, aerosols containing combustible dusts or liquids. Importantly, this mechanism occurs both for materials with densities close to the theoretical densities and for systems with densities equal to fractions of the TMD. The mechanism of this process depends on the system in which it occurs; in low density systems and gases, effects related to turbulence and diffusion of reaction products predominate, while in low porosity solids the increase in pressure leading to DDT is associated with laminar burning [36, 38]. Paper [36] points to these two models as the main DDT models, described as DDT1 and DDT2, respectively. A key factor affecting the dominant transition mechanism is the density and porosity of the high-energy material. The authors of the paper [36] indicate as a limit value a density of about 50-70% TMD, depending on the specific system.

The DDT model was first described by Macek and co-authors in [39]. In paper [40], this model was confirmed by more accurate models. However, a number of objections to Macek’s model have been presented [41]. According to Macek’s model, for a high-energy material in a sheath which restricts the movement of the products of combustion, when ignited from one of the outlets at the combustion front, there is a pressure increase which generates acoustic waves (compression waves) in the products of combustion with a velocity

equal to the velocity of sound in the medium. This leads to an acceleration of the burning front which generates further waves of compression in the unreacted explosive. According to this model, overlapping waves lead to the formation of a discontinuous surface (known as a piston), which accelerates until a detonation wave is generated. This mechanism is limited by the need to restrict the scatter of explosion products which ensures that the pressure rises to a level which enables the formation of a shock wave, and by the rapid nature of the pressure rise, which must be fast enough to allow subsequent compression waves to “catch up” [37, 41].

Of interest from the point of view of high-energy transitions of NSTEX compositions is the DDT2 mechanism. According to papers [36, 37], this mechanism is characteristic of solid explosives with low densities and high porosity, and of aerosols. After EM ignition and the conduction-limited combustion stage, the generation of hot gaseous products and their diffusion deep into the EM column leads to the transition of the process to convection-limited combustion. The gaseous products of the transition thicken the material before the burning front, leading to a decrease in porosity and reducing further gas flow. In this way, the gases form a confined column, where ignition is further initiated only at the boundaries of the column. The continuous increase in temperature and pressure results in an increase in burning rate, leading to a localised thermal explosion, generating a shock wave. This shock wave has sufficient parameters to initiate an SDT. The initial detonation velocity over a short distance is characterised by a higher value than that corresponding to the initial density of the material, as confirmed by the densification of the material described above [42].

The occurrence of a DDT1 or DDT2 process depends on parameters such as the type of explosive, the rate of burning in the bare state, the fragmentation and proportion of the different fractions, the morphology of the particles, the configuration of the charge – the envelope material, its dimensions and the method of initiation [36, 37].

4. High-energy transitions of NSTEX compositions

In paper [31], the authors studied the DDT process of a composition consisting of two RDX grades (coarse crystalline G-RDX and fine crystalline D-RDX; the authors do not specify the grade or grain size characteristics) and Al/Fe₂O₃ nanothermite containing 38.4% fuel. The composition preparation process was carried out in such a way that the RDX grains were uniformly coated with nanothermite to obtain a structure similar to a core/shell (quasi-core/shell) arrangement. The high-energy transitions of these compositions were investigated by the authors using a fixed-volume manometric bomb and using a so-called DDT-tube. For the DDT-Tube test, the test compositions were elaborated into a steel cylinder 300 mm long and 18×5 mm in diameter. The density of the compositions tested ranged from 0.54-0.60 g/cm³. A schematic diagram of the DDT-Tube test system is shown below (Figure 2).

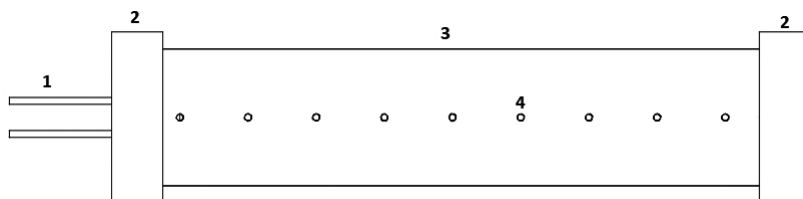


Figure 2. A schematic diagram of the DDT-Tube system, where (1) igniter wires, (2) plugs, (3) body, (4) ionisation pins (based on [31])

When measured in a manometric bomb, the time to reach the maximum overpressure decreases with increasing nanothermite proportion in the composition. At the same time, the rate of pressure build-up and maximum overpressure increases. The relationships obtained are analogous for both RDX grades. A clear

increase in the values of the measured parameters is seen for compositions based on D-RDX, with the rate of pressure build-up increasing from 0.429 MPa/ μ s for pure hexogen to 2.527 MPa/ μ s for a composition containing 50% nanothermite.

Also, an examination of the development of the DDT process indicates a rapid acceleration of the process as the nanothermite content of the tested composition increases. Increasing the nanothermite content to 30% in the composition shortened the distance of stable detonation development from 9.5 cm (for G-RDX) and 8.5 cm (for D-RDX) to just 2.5 cm. Graphs describing the time dependence of the front position for a series of NSTEX-type compositions are shown below (Figure 3).

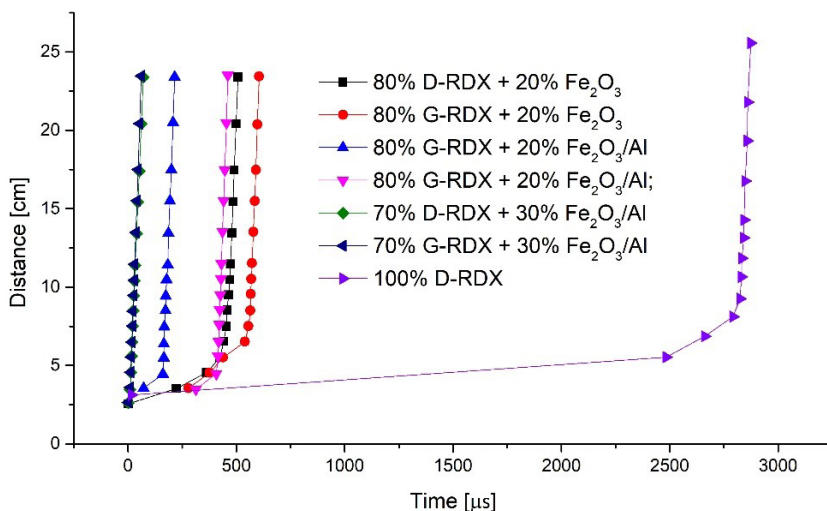


Figure 3. Curves describing the development of the detonation process of the NSTEX composition (based on [31])

The authors of the paper indicate a process similar to DDT type II. The main difference in the propagation mechanism is related to the coverage of the RDX grains by the nanothermite. The burning rate of nanothermites reaches 2500 m/s, whereas the burning rate of HE does not exceed a few m/s. As the hexogen grains are coated with nanothermite, the initial slow burning process is rapidly accelerated by the nanothermite, which initiates the ignition of subsequent hexogen grains and generates significant amounts of heat. This leads to a more rapid increase in pressure and temperature to a level which enables a stable detonation process to be initiated. According to the authors, however, the heat generated by the nanothermite does not fuel the propagation of the detonation wave once the stable detonation regime is stabilised, due to the much slower reaction rate. The decrease in detonation velocity with increasing nanothermite content is related to the absorption of some of the shock wave energy by the nanothermite [12]. However, it should be borne in mind that the research was conducted for very low-density systems, as an increase in density strongly slows down the burning processes of nanothermites, and it is difficult to estimate whether such an effect will be observed for such a system. The effect of nanothermite burning on shock wave propagation is ambiguous, as the maximum burning rates of nanothermites reach values typical of low detonation velocity explosives. In paper [43], the authors investigated the high-energy parameters of Al/CuO nanothermites, differing in the parameters of the oxidant used, and their mixtures with AN, Cl-20 and RDX. All NSTEX compositions were prepared by ultrasonic dispersion, nanothermite with a high-energy additive in 2-propanol and drying. For the compositions in question, the authors determined the pressure profiles and propagation velocity of the high-energy transition. The authors carried out the testing of the hybrid compositions in a manometric bomb with a chamber volume of 0.06 cm³ and for EM amounts of 20 mg.

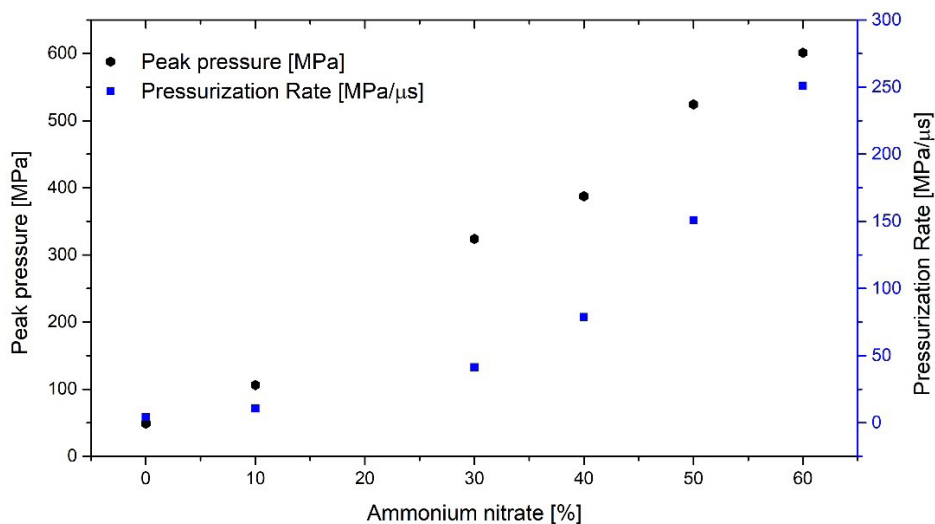


Figure 4. Maximum overpressure values and pressure build-up rates (based on [43])

In the discussed studies, the authors used a nanometric AN prepared using the antisolvent method. With an increase in the AN content of the composition, there is an increase in the maximum overpressure and the rate of pressure build-up. This increase is particularly evident for compositions containing more than 30% AN. This is associated with a change in the limiting stage of the propagation of the high-energy process. The dominant effect limiting the decomposition of the entire composition is then the decomposition of AN, in place of the burning of nanothermite.

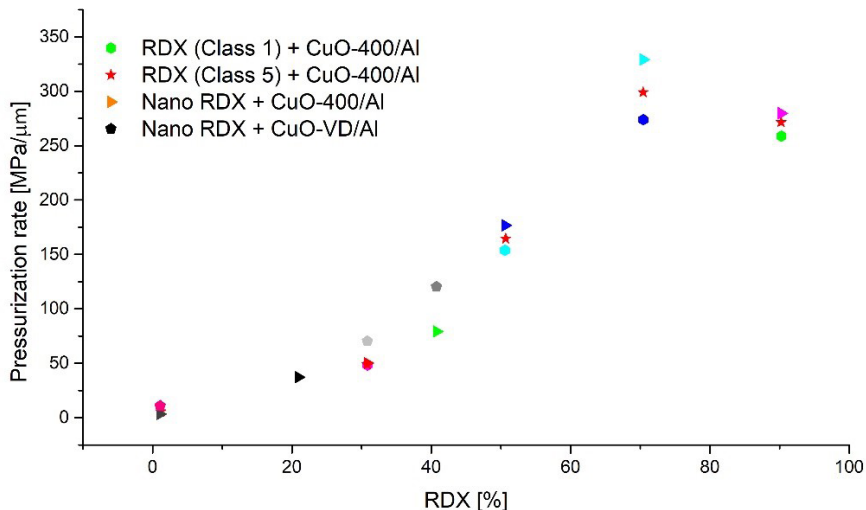


Figure 5. Pressure build-up rates of NSTEX compositions (based on [43])

The results of analogous tests for compositions containing RDX (with nanometric fragmentation, class 5 equivalent and class 1 equivalent), are shown in Figure 5. For compositions containing the addition of RDX or CI-20, the authors distinguished between three possible stages of the high-energy process, differing

in the limiting step of the decomposition process. Analogous to AN-containing hybrid compositions, decomposition is initially limited by nanothermite burning, followed by EM decomposition. The authors also distinguish between a “mixed regime”, i.e. a regime in which the process is constrained by both nanothermite and incomplete reaction of EM. In both compositions containing RDX and Cl-20, the highest maximum overpressure and the highest rate of pressure build-up were recorded for a 70% EM content. The values of these parameters decreased depending on the RDX used in a range of nanometric RDX, RDX class 5, RDX class 1 [44]. Significantly, the experiments in question were conducted in a volume-limited chamber. When the aforementioned compositions were initiated in open space, they burned slowly, not developing into a violent high-energy reaction.

The authors of the discussed study investigated the propagation velocity of the high-energy transition by initiating the compositions studied in polycarbonate tubes with lengths of, sequentially, 10.16; 20.32 and 30.48 cm. The density of the compositions tested was in the range 0.85-0.95 g/cm³. Studies have shown that by increasing EM content, the propagation velocity increases rapidly and the process stabilisation time decreases. Analogous to the pressure profile analysis, the authors point to different mechanisms of process propagation, depending on the EM content. It should also be noted that an increase in RDX content from 30% to 50% more than doubles the propagation velocity, which also indicates a change in the mechanism regulating this process in this range of EM content.

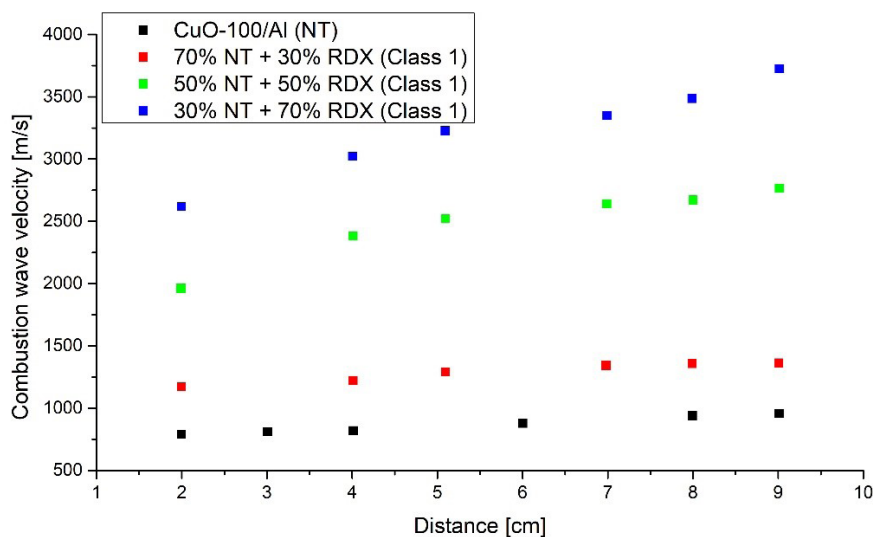


Figure 6. Development of the high-energy process as a function of charge length (based on [43])

In the paper under review, the authors described the design of a variable volume manometric bomb. Based on general thermodynamic relations, the authors determined the heats of combustion reaction of the compositions tested versus change in volume of the manometric bomb. On the basis of this study, the authors concluded that the heat of reaction increased as the volume of the manometer chamber increased. The authors point to a reduction in heat loss as the main explanation for this phenomenon, due to an increase in the ratio of the volume to the surface area of the test chamber walls.

In paper [30], the authors investigated the development of a high-energy process in compositions consisting of RDX (nanometric and class 1), with the addition of Al/WO₃ or Al/Bi₂(SO₄)₃ nanothermites with a fuel/oxidant ratio of 50:50. The compositions were prepared by physical grinding and mixing using a Vortex-type mixer. Compositions of 100 mg were elaborated into plastic sleeves, 25×11 mm in diameter and 150 mm long. An Al/CuO nanothermite was placed on a section of 5 mm from the ignitor side.

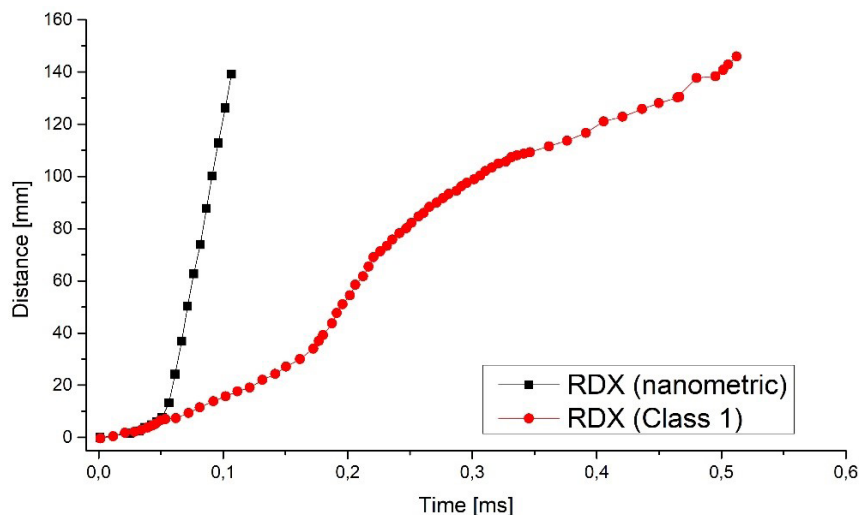


Figure 7. Development of the high-energy process as a function of charge length (based on [30])

Figure 7 shows the position of the front versus time for a composition containing 60% RDX. The initial propagation velocity corresponds to the action of the ignition Al/CuO composition. In the case of a composition containing Class 1 RDX, fluctuations in burning rate associated with pressure changes due to envelope damage are evident. Confirmation of the process taking place, in the form of deflagration, is provided by a series of images captured with a high-speed frame camera [30]. In the case of a composition containing nanometric RDX, a rapid acceleration of front propagation velocity is observed, leading to detonation in the stable regime ($D = 2529$ m/s). Images captured by the high-speed frame camera confirm the formation of a stable detonation wave.

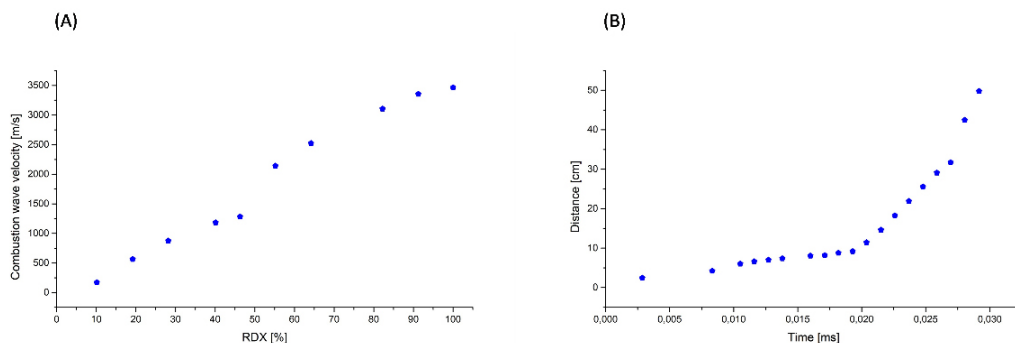


Figure 8. Flame propagation velocity versus RDX content (A), development of the high-energy process in the system under study (B) (based on [30])

Figure 8A shows the variation of the process propagation velocity with RDX content. As a result of the study, the authors noted the development of combustion to detonation in samples containing nanometric RDX. The distance over which the burning to detonation transition occurred, depending on the RDX content, was in the range 0.8-3 cm. Depending on the RDX content, process propagation velocities ranged from 170 m/s (for pure nanothermite) to 3500 m/s (for pure nanometric RDX). The absence of a DDT process for compositions containing micrometric RDX is most likely related to the significantly lower

porosity, which also fluctuates strongly depending on the nanothermite/RDX ratio. In the case of nanometric RDX, the authors specify the porosity as constant, equal to approximately 83%. It should also be borne in mind that with decreasing EM grain size the sensitivity to shock wave increases and the critical diameter decreases, but at the same time the sensitivity of EM to flame decreases [9]. The authors also demonstrated an increase in detonation velocity with increasing composition density, which also confirms the occurrence of a process in the form of stable detonation. At the same time, the aforementioned paper investigated the ability of the compositions in question to initiate a PETN charge of 200 mg and a density of 1.7 g/cm³ in the following arrangement: Al/CuO nanothermite – NSTEX test composition – PETN charge. The results of the aforementioned tests are presented in Table 1 and Figure 8 (B) shows an example of the process development.

Table 1. Ability of the compositions tested to initiate a PETN charge [30]

Composition	FPV [m/s]	TMD [%]	PETN detonation
WO ₃ /Al/nano-RDX (12.4/27.6/60)	3050	29.1	Yes
	3113	27.1	Yes
	2831	14.4	No
Bi ₂ (SO ₄) ₃ /Al/nano-RDX (20/20/60)	3189	30.2	Yes
	3115	26.8	Yes
	3302	27.3	Yes
	2765	16.1	No
	2472	14.5	No

In both cases, compositions with a density of less than 27% TMD and a detonation velocity of less than 3000 m/s did not initiate detonation of the secondary PETN charge. Despite the slight difference in recorded front velocity, the decrease in composition density also implies a decrease in the energy density released by the process, which affects the initiating capacity.

In paper [34], the ballistic pendulum method was used to compare the workability of TNT and TNT-containing compositions with the addition of nanometric Al, nanothermite Al/CuO or nanothermite Al/CuO/MWCNT (the Al/CuO ratio in each case was equal to the stoichiometric ratio). After preparation of the nanothermite compositions by ultrasonic dispersion, they were added to the molten TNT matrix. The paper showed a significant increase in workability of around 30% for the Al/CuO/TNT compositions, relative to pure TNT and Al/TNT compositions. Compositions containing the addition of MWCNT showed parameters intermediate between pure TNT and Al/TNT compositions. The authors investigated the flash point of the composition and determined the value of the total heat released as a result of the decomposition using DSC; the results are shown in Table 2. Already the addition of nanometric Al caused a sharp increase in the total heat released during the heating of the sample, and a reduction in the temperature corresponding to the maximum heat flux by 37 K. This effect is more pronounced for the addition of Al/CuO nanothermite, where the corresponding temperature is 50 K lower compared to pure TNT.

Table 2. Results of tests using DSC [34]

Composition	Total heat released [J/g]	Increase in heat relative to TNT [%]	Temperature at maximum heat flow [K]
TNT	520	–	565
Al/TNT	925	78	528
Al/CuO/TNT	1213	133	515

In paper [45], the authors performed a workability study using the ballistic pendulum method for the Al/MnO₂/TNT composition. The ratio of fuel to oxidant in the nanothermite composition was stoichiometric.

Nanothermite was mixed with molten TNT after ultrasonic dispersion in 2-propanol. The results of the work show a 35% increase in workability.

In paper [46], the authors performed a Kast (copper cylinder crush) test to determine the brisance of the compositions tested consisting of TNT, with possible addition of Al/Fe₂O₃ or Al/CuO nanothermites. Analogous to previous work, nanothermite was mixed with liquid TNT after ultrasonic dispersion in 2-propanol. The addition of nanometric Al or nanothermite clearly increased the brisance of the EMs tested relative to pure TNT. The results of the test are shown in the figure below (Figure 9).

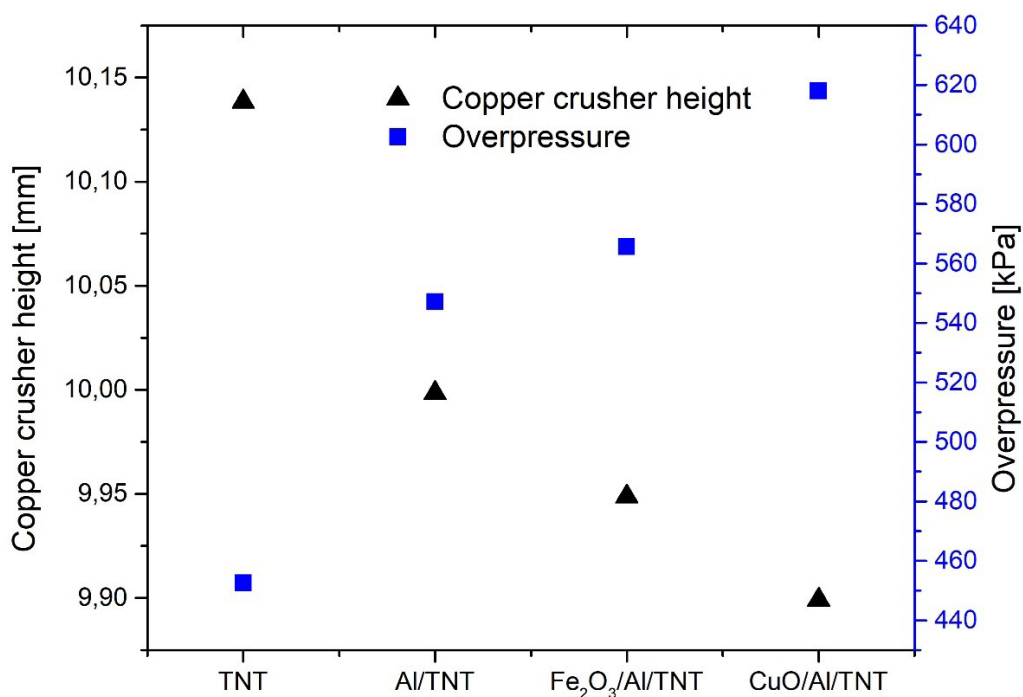


Figure 9. Brisance test results (based on [46])

Significantly, the authors of papers [34, 45, 46] point out that the increase in high-energy parameters is related to the occurrence of a burning reaction of the nanothermite in the area of the detonation wave which increases its parameters. This conclusion contradicts the conclusions of paper [43].

5. Summary

- ◆ Compositions such as NSTEX show properties which allow them to be considered as replacements for, inter alia, initiating explosives based on lead compounds. The work presented above demonstrated the detonation capability of these compositions, confirmed the occurrence of a DDT2 process, a reduction in detonation path and scatter time relative to pure HE, an increase in workability, heat of explosion and brisance.
- ◆ The sensitivity of the compositions in question to initiation stimuli is sufficient for the potential applications discussed in this paper, while at the same time the wide range of possibilities to change the composition allows a compromise to be made between sensitivity and work safety. An important feature of the above-mentioned compositions is the possibility of developing compositions with selectively enhanced sensitivity to stimuli such as laser radiation of a given length or electrical discharge.

- ◆ The lack of consensus on the propagation mechanism of the high-energy process should be noted. The addition of nanothermite partially alters the mechanism due to the high linear burning rates and high reactivity. The percentage of nanothermite in a NSTEX-type composition influences the mechanism limiting the development of the high-energy process, the velocity of detonation and the time required for a stable detonation process to establish itself. Also problematic in this context is the fact that there is no accurate model describing the burning process of the nanothermites themselves, and the variation in the compositional properties of this group makes a comprehensive analysis of this issue difficult.
- ◆ A contentious issue is whether the nanothermite burning process occurs in the detonation wave region. Reduction in detonation velocity, related to the absorption of the detonation wave energy by the nanothermite, which does not completely exclude a simultaneous reaction at the detonation front. The increase in brisance and workability is not a sufficient effect to unambiguously assess and characterise the processes occurring in the detonation wave area. Extending possible further research to include techniques such as the cylinder test, underwater explosion test or electromagnetic mass velocity measurement, can provide data accurately characterising the high-energy transition and its parameters.
- ◆ The advantage of NSTEX compositions is the considerable number of methods of obtaining and elaborating them, hitherto difficult for typical IEMs. Techniques such as electrospraying, electrospinning, 3D printing or electrodeposition open up entirely new possibilities for the design of EM properties, shaping into utility forms, explosive device design and possible applications.
- ◆ There are few papers addressing the long-term chemical and physical stability of NSTEX compositions. However, lower stability and resistance to environmental conditions, relative to typical IEMs, should be expected. The lowering of the flash point, relative to pure HE, simultaneously includes a reduction in thermal stability. The addition of nanothermite to HE leads to a lower flash point relative to the initial HE. The price of such materials, which is considerably higher than that of classical IEMs, may narrow their application potential to special products or to applications in areas where this will be enforced by regulations restricting the use of harmful compounds. However, it is expected that there will be increasing interest from the scientific community in this topic.

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