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# Combustion of Energetic Systems Based on HMX and Aluminum: Influence of Particle Size and Mixing Technology

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**Abstract:** In this work the complex experimental investigation of the microstructure and burning parameters of HMX-monopropellant and 25%Al/75%HMX energetic systems was carried on with the particle size variation. Components, their mixtures, pressed samples, and the combustion products (agglomerates) collected from a burning surface by QPCB (quench particle collection bomb) technique were investigated. Two types of HMX particles: micro-sized (mHMX) and ultrafine (uHMX) and aluminium powders: micro- and ultra-sized (ALEX™) were used. Morphology and particle size were examined by atomic-force microscopy (AFM), scanning electron microscopy (SEM) and BET-analysis. AFM analysis shows the ALEX™ average volume particle size is 180 nm. It was shown, that the monopropellant's burning rates of the micro- and ultra-sized HMX are almost identical in the pressure range 20-100 atm. Two mixing technologies to prepare Al/HMX compositions were used: (i) conventional "dry" mixing and (ii) "wet" technique with ultrasonic processing in diethyl ether. Applying of ultrasonic technique results in a burning rate increase up to 18% comparing to "dry" mixing (under pressure 60 atm). The highest combustion rate was determined for composition of mHMX/ALEX™ (porosity 13%). Influence of component's

size and composition's microstructure on the burning rate of energetic systems is discussed and analyzed.

**Keywords:** energetic systems, burning rate, HMX, aluminium

## Introduction

One of the key problems of the rocket development is still a problem of the energetic condensed systems (ECS) improvement. Alone with the new materials elaboration, the growing attention is paid to "upgrading" of the existing high-energy components by decreasing the particle size and changing a physical and/or a chemical state of the particle surface. According to the literature, the intensive study of the nano-sized high-energy components and compositions with nano-components shows that the burning rate could be sufficiently increased for these compositions in comparison to the systems with conventional components. At the same time, the pressure dependency of the burning rate, the ignition time delay, and agglomeration phenomena could be decreased. To evaluate agglomeration phenomena the QPCB technique was proposed [1].

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine ($C_4H_8N_8O_8$) is known as HMX, and it is one of the most important energetic ingredients used in various propellants and explosives. HMX-containing compositions have high mass-energy characteristics. Such systems have many advantages (high density, potentially high specific impulse) but their combustion characteristics are somewhat non-ideal. It was observed [2] that, for a given HMX-energetic binder composition, the burning rate law is locked and that there is no way to tailor it (as can be done in AP-inert binder compositions by acting upon the particle size). Furthermore the pressure exponent is too high to be acceptable for the motor operation. Attempts to act upon the HMX burning rate by the use of additives have not been successful. However, the possible action is to tailor the gas-phase zone, where the highest energy-release takes place. One of the techniques to influence the stand-off distance is an addition of aluminium powder.

Aluminium is one of the main components in propellants, with the general content of about 20%. Many factors, such as the content and particle size of aluminium powders and its spatial localization can influence the combustion characteristics of these compositions. One of the important parameters for the specific impulse loss is a chemical incompleteness of aluminium burning. To evaluate this value we study morphology and chemical composition of the combustion products.

Beckstead [3] reported that the burning rate has a relatively low dependency on the HMX crystal size, whereas for AP-based composition this dependency is very strong. The HMX particle size distribution and morphology are important parameters in understanding and modelling the microstructural response of this material to external stimuli.

Recently, the cryochemical technique to synthesize the ultra- and nano-sized crystalline compounds was reported [4], and some high-energy components were successfully fabricated. The question arises, whether the use of ultrafine and nano-sized components has a benefit for energetic condensed systems.

Ignition tests of HMX, by exposing the sample to a given surface heat flux and detecting the delay for the first exothermic ignition reaction (rapid deviation of the surface temperature from that of an inert material) confirm results obtained by DTA [5]. That is why we used DSC/TG analysis to study the thermal behaviour of micro-sized and ultrafine HMX powders.

This article is focused on the study of morphology and combustion parameters of HMX-based composition with aluminium with the particle size variation.

## Experimental

### Materials

To determine metal particle influence on combustion parameters two different aluminium powders were investigated: ultrafine aluminium powder ALEX$^{TM}$ (Argonide Corporation, USA) and micro-sized spherical aluminium ASD-6.

Particles morphology, thermal behaviour, and monopropellant burning rate were examined for ultrafine HMX, synthesized by cryochemical technique, and conventional HMX.

Complex comparative study was conducted for binary compositions with 25 wt% of aluminium and 75 wt% HMX, as shown in Table 1.

**Table 1.** Nomenclature of investigated compositions

| Nomenclature | Composition |
|---|---|
| mHMX | 100% micro-sized HMX |
| uHMX | 100% ultrafine HMX |
| mAl-mHMX | 25% micro-sized Al + 75% micro-sized HMX |
| mAl-uHMX | 25% micro-sized Al + 75% ultrafine HMX |
| uAl-mHMX | 25% ultrafine Al + 75% micro-sized HMX |
| uAl-uHMX | 25% ultrafine Al + 75% ultrafine HMX |

**Equipment**

A theoretical evaluation of the adiabatic temperatures for studied ECS was conducted using the TERMPS computer code.

To investigate materials morphology scanning electron microscopes Phenom and Quanta 200 3D (FEI, USA) were used. Microscope Quanta 200 3D was equipped with an energy dispersive spectrometer (EDS).

Atomic force microscopy (AFM) images were recorded with NTEGRA Prima (NT-MDT, Russia) operated in a tapping mode at ambient conditions. Cantilevers Tl02 (MikroMash, Estonia) with curvature radius less than 10 nm were used.

The BET surface area was determined with FlowSorb III 2305 (Micromeritics, USA) by measuring adsorption of gas mixture (30%$N_2$/70%He) on powder surface.

Investigation of thermal behaviour was carried out using the DSC/TG simultaneous thermal analyzer STA 409PC (NETZSCH, Germany). The nominal heating rate of 2-10 °C/min (covering the temperature range from 20 to 1100 °C) was employed using samples size of 2 mg (for agglomerates – 100 mg) in a dynamic argon flow (35 ml/min). Calibrations of TG mass, DSC baseline, and temperature were conducted before the experiments.

Thermal analysis was used to determine the aluminium content within initial Al powders and within agglomerates collected during combustion of binary samples Al/HMX. Specially elaborated comparative technique based on analysis of endothermal melting peak of reference Al sample and the sample under study was applied.

Ultrasonic probe SONOPULS HD2070 (Bandelin, Germany) was used for preparing compositions by "wet" mixing technique at 60% of maximal power (70 W) and frequency of 20 kHz.

The experimental investigations of burning rate were performed using a constant pressure bomb in nitrogen atmosphere. The calculated average accuracy of the burning rate measurements is ±3%. The sample pellets were cylindrical (8 mm in diameter) for burning rate experiments and rectangular for agglomeration collection. Due to the quartz windows, the combustion process was recorded for the subsequent digitizing. To collect the combustion products with metal-containing agglomerates from the burning surface QPCB technique (quench particle collection bomb) [1, 6] was used.

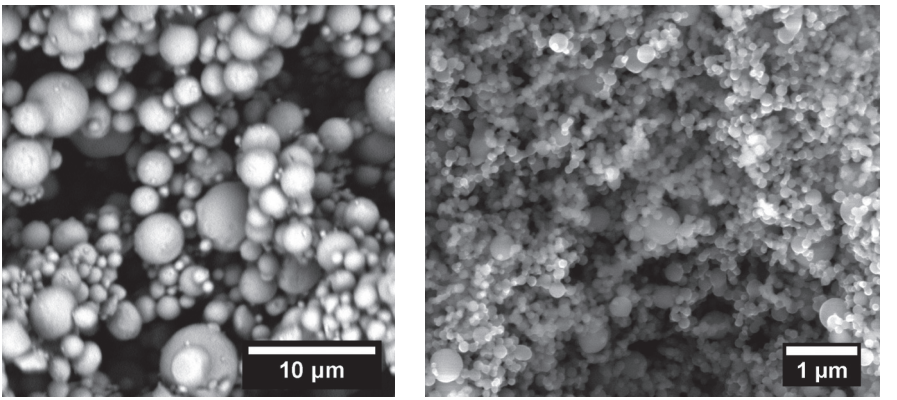
## Results and Discussion

### Initial components

**Aluminium**. By analysis of AFM images of ultrafine aluminium particles-size distribution was obtained. The particles of ALEX$^{TM}$ (Argonide Corporation, USA) powder are ideally spherical with an average volume diameter $D_{43}$ of 180 nm. As it is shown in Table 2, obtained BET surface area is 11.9 $m^2/g$ (corresponds to an average surface diameter $D_{32}$ of 190 nm) and agrees with literature data [8, 10]. Aluminium content was obtained by two independent techniques: by endothermic effect of melting in argon atmosphere (DSC-curve) and by EDS. Both results reveal 84% of active aluminium content for ALEX$^{TM}$, as shown in Table 2.

Particles of micro-sized aluminium are also spherical with an average volume diameter, of 3.3 μm, as was obtained from the SEM-images (Figure 1a) particle-size distribution. There is a difference between obtained diameter and values from literature [9, 10]. Note, that we used a numerical particle-size distribution, whereas authors [9, 10] examined a weight distribution. Average surface diameter from BET surface area (1.4 $m^2/g$) is 1.6 μm. Percent of metal aluminium is equal to 94.7%.

Table 2 represents the distribution characteristics (<D> is average linear diameter), BET specific surfaces and the active aluminium contents of the investigated ultrafine and micro-sized powders in comparison to the literature data.




a) b)

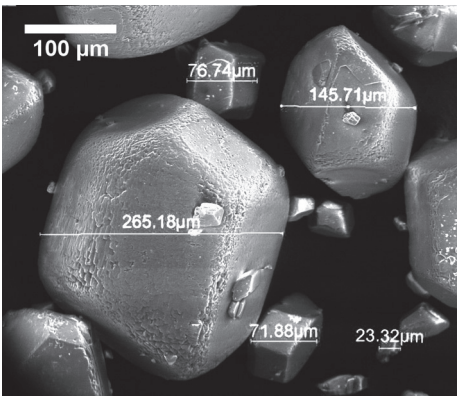
**Figure 1.** SEM images of aluminium particles: a) micro-sized (ASD-6) b) ultrafine (ALEX$^{TM}$).

**Table 2.** Aluminium powders characteristics

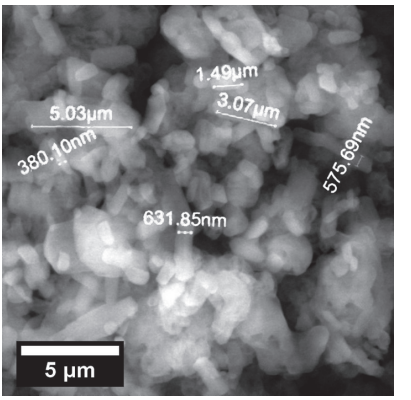
| Powder type | <D>, μm | $D_{32}$, μm | $D_{43}$, μm | $S_{BET}$,$m^2$/g ($D_{32}$, μm) | Active Al, % |
|---|---|---|---|---|---|
| **Micro-sized (ASD-6)** | 1.4 | 2.7 | 3.3 | 1.4 (1.6) | **94.7** |
| ASD-6 [10] | 0.85 | | 4.72 | 0.739 | |
| ASD-6 [9] | 4 | 5.2 | 6.5 | | |
| Ultrafine (ALEX™) | 0.12 | 0.17 | 0.18 | 11.9 (0.19) | **84** |
| ALEX™ [10] | 0.12 | 0.16 | 0.18 | 13.889 | |
| ALEX™ [8] | | | | 12.1 | |

**HMX**. SEM image of conventional powder is shown in Figure 2a. Micro-sized HMX consists of large crystals of regular shape. Microscopy reveals that the average projected diameter value is 65 μm. Effective size from BET surface area is 11 μm.

Figure 2 presents the structure of ultrafine octogen powder: SEM image of as-received powder (Figure 2a), AFM-image of pressed pellet surface (Figure 2c,d). Ultrafine octogen powder has a complex structure with at least three levels: conglomerates of submicron particles with the average size of 10 μm (Figure 2b), submicron particles (Figure 2c), which in turn consist smaller particles of several hundred nanometres (Figure 2d). BET surface area for ultrafine HMX is 1.9 $m^2$/g, which corresponds to effective diameter 1.6 μm.




a)

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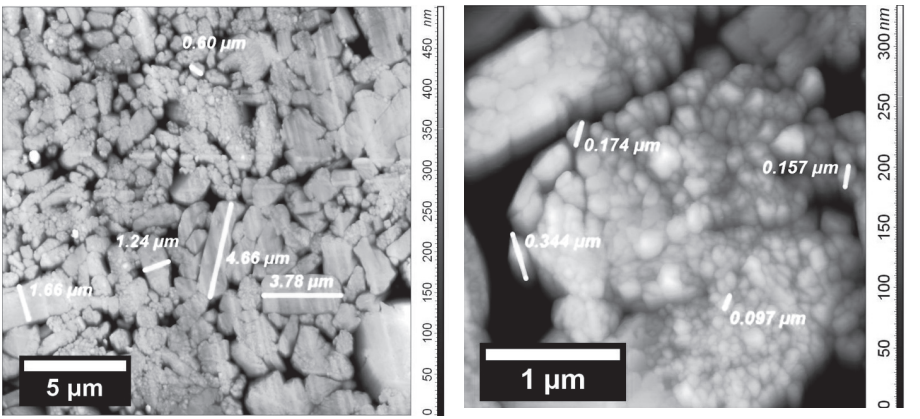



c) d)

**Figure 2.** SEM (a,b) and AFM (c,d) images of HMX: a) micro-sized; b) - d) ultrafine.

**Thermodynamic calculation**

For pressure 60 atm thermodynamic properties of Al/HMX composition with various aluminium percents were calculated. The maximal adiabatic temperature (Figure 3) and local maximum of the condensed phase mass fraction are obtained at 20% of aluminium. Volume fractions of gaseous products are presented in Figure 4.

The specific impulse ($I_{sp}$) values of Al/HMX composition with various aluminium concentration were calculated with an optimum expansion from 60 atm to 1 atm taking into account the alumina content in powders. The metal activity values of micro-sized and ultrafine Al powders were determined by thermal analysis. At 25% Al content the specific impulse of composition with micro-sized metal is equal to the one with ultrafine aluminium and to $I_{sp}$ of HMX monopropellant (Figure 5).

For further investigation the composition 25% Al/75% HMX was selected. At this aluminium content we have a little loss in an adiabatic temperature, but the fraction of gaseous products with high molar mass (*i.e.*, $CO_2$, $H_2O$) is much smaller than for stoichiometric mixture.

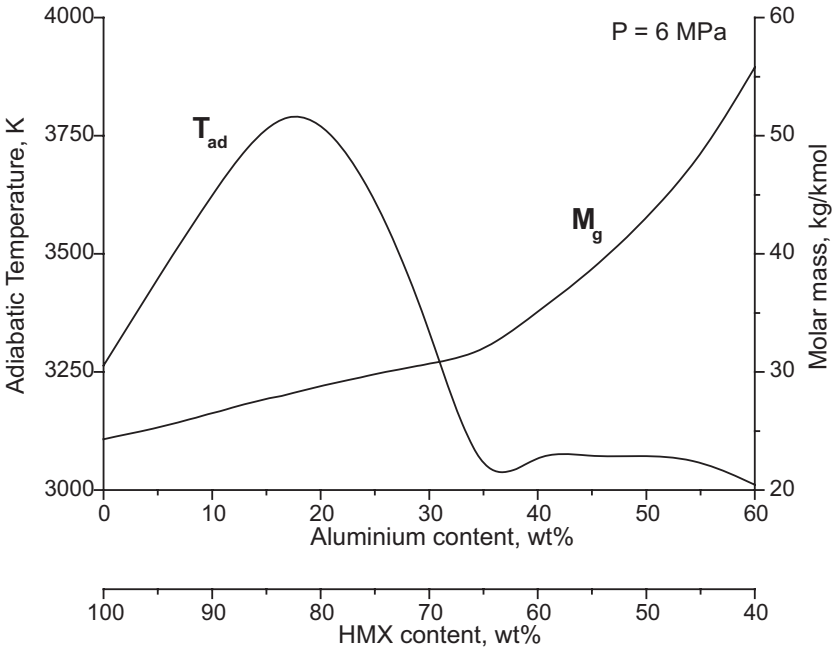



**Figure 3.** Adiabatic temperature and molar mass of combustion products.

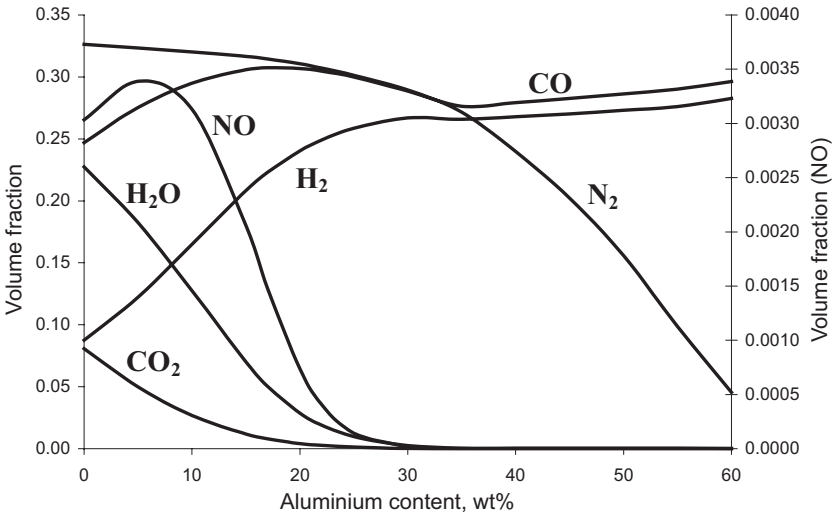



**Figure 4.** Volume fractions of gaseous products.

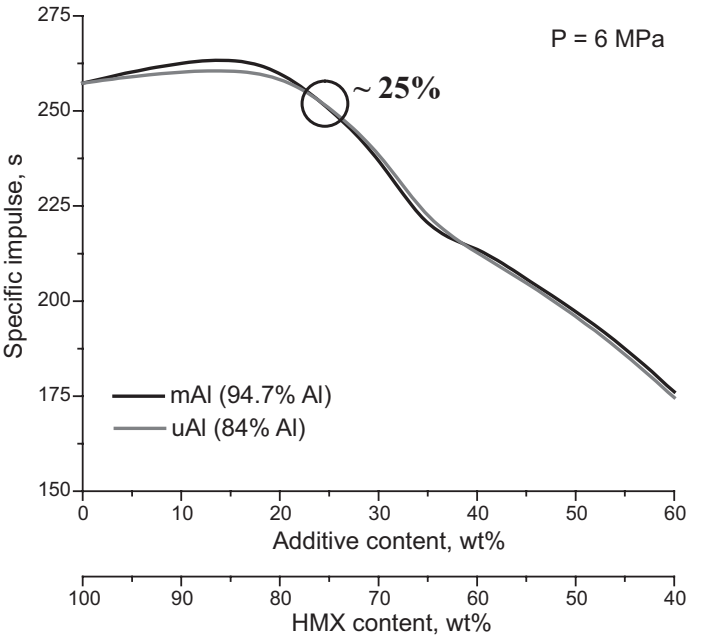



**Figure 5.** Specific impulse for Al-HMX systems.

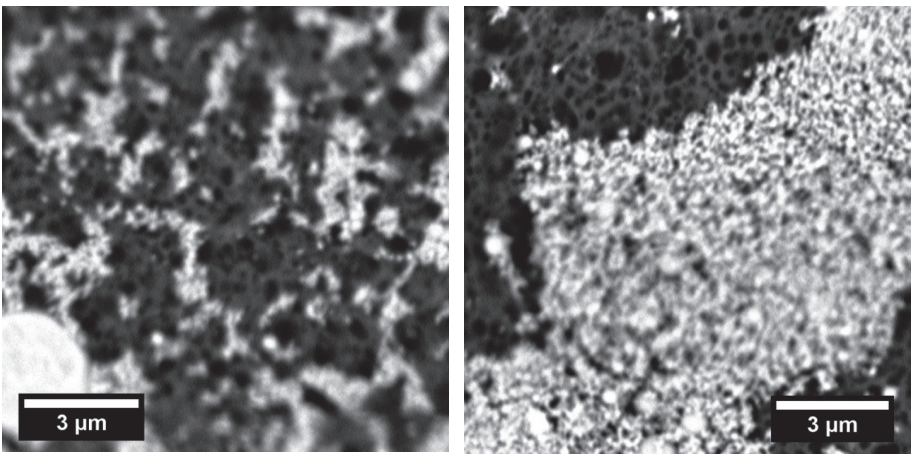
**Binary compositions**

Initial components were mixed by conventional "dry" process (mixer "Turbula" type, time of process – 1 hour, mass of load – to 10 g). After mixing, samples were pressed by cold isostatic technique into cylindrical pellets.

Figure 6 represents SEM images of the pressed pellets surface of aluminium-HMX compositions. We used SEM with back-scattered detector, which allows obtaining "phase contrast". Thus, the lightest component on the SEM-images of Al/HMX composition is aluminium.

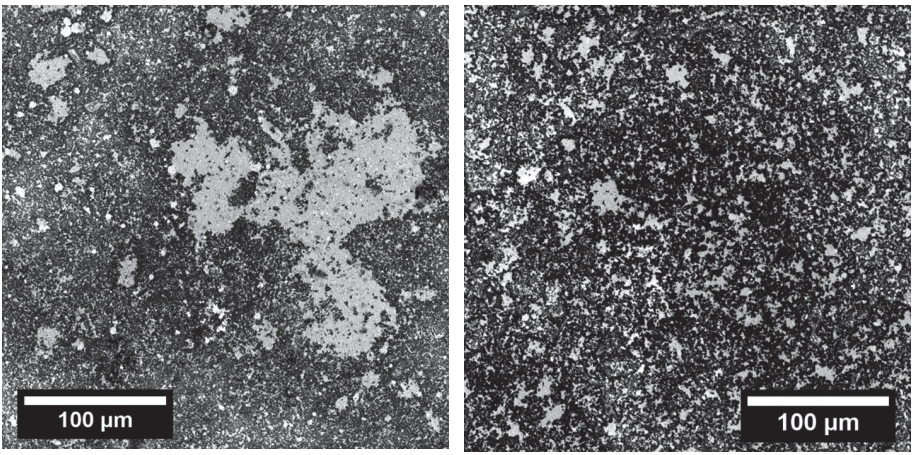
Analysis of SEM-images of the Al/HMX surface reveals that the mixture of ultrafine components has much more uniform spatial distribution of aluminium comparing to mixture with micro-sized components. However, this uniformity is quite far from the ideal mixing – the amount of aluminium particles between HMX crystals is still very high.

To improve the mixture uniformity, the ultrasonic process was elaborated and applied (so called "wet" mixing). Components were mixed in diethyl ether under ultrasonic processing during 30 minutes, obtained slurry was dried for 30 minutes under vacuum. After drying reactant mixture was pressed into samples.




a) b)

**Figure 6.** SEM images of pressed pellets: a) uAl-uHMX; b) uAl-mHMX (white particles – aluminium).




a) b)

**Figure 7.** SEM images of pellet's surface of system with ultrafine components: a) conventional, b) "wet" mixing.

Figure 8 shows the BET surface area values of the final mixtures in comparison to the calculated as additive function surface area. Surface area is about the same for both investigated mixing techniques ("wet" and "dry" ones), and in turn about equal to the calculated surface area. This result reveals that no particles fragmentation/conglomeration occurs during mixing.

SEM images shows that "wet" mixing (Figure 7b) leads to enhanced homogeneity of compositions, comparing to "dry" technique (Figure 7a).

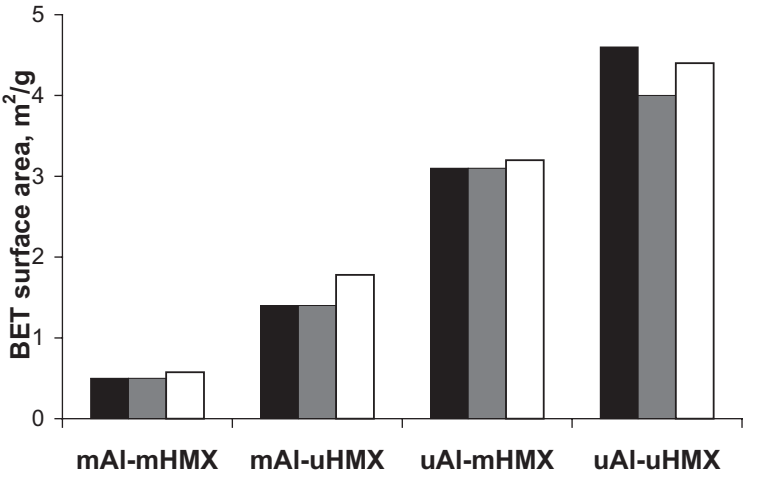
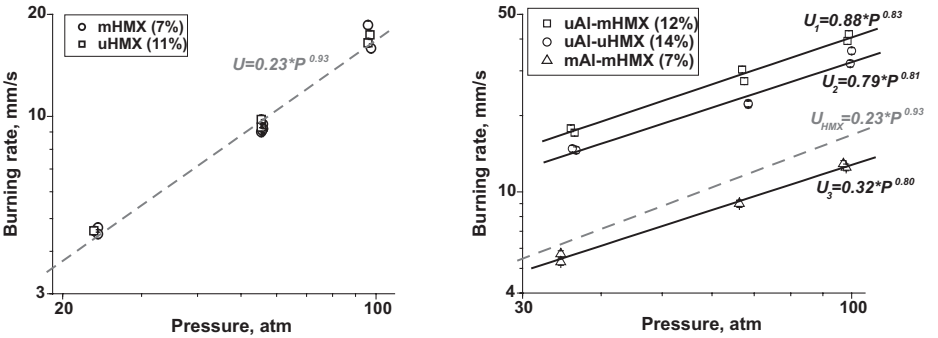



**Figure 8.** BET surface areas of Al/HMX mixtures as result of "dry" (black bars) and "wet" (grey bars) mixing technologies and calculated values (white bars).

**Combustion parameters**

**Burning rate**. Monopropellant burning rate was measured under nitrogen in the pressure range 30-100 atm. Two types of HMX particles, i.e., micro-sized and ultrafine powders show identical U(P) dependencies, as presented in Figure 9a (log-log plot). The average density of the micro-sized samples was 1.82, whereas for the samples of ultrafine HMX − 1.74 g/cm$^3$. The load increase of micro-sized HMX monopropellant from the sample density 1.8 to 1.89 g/cm$^3$ did not result in a noticeable burning rate change. Experimental burning rate law thus obtained is $U=0.23*P^{0.93}$.

Table 3 illustrates good correlation of U(P) dependency with the literature data [11, 12]. Figure 10 presents our experimental results (dashed line) in comparison to numerous literature data [11-22] of the HMX(β) monopropellant burning rate. Note, that the most of the literature data were obtained for HMX sample density of 1.7-1.72 g/cm$^3$ with the exception of data [11, 17], where the monopropellant sample density is 1.89 g/cm$^3$.




a) b)

**Figure 9.** a) Micro-sized and ultrafine HMX burning rates from pressure; b) Burning rates for Al/HMX: uAl-mHMX ($U_1$), uAl-uHMX ($U_2$), mAl-mHMX ($U_3$), and monopropellant (dashed line).

**Table 3.** Burning law parameters for HMX monopropellant ($U=B*P^{\nu}$)

| B | ν | Note |
|---|---|---|
| **0.23** | **0.93** | This article |
| 0.23 | 0.89 | 1.7 g/cm$^3$; 3-401 atm [11] |
| 0.21 | 0.91 | 1.91 g/cm$^3$; 36-104 atm [12] |

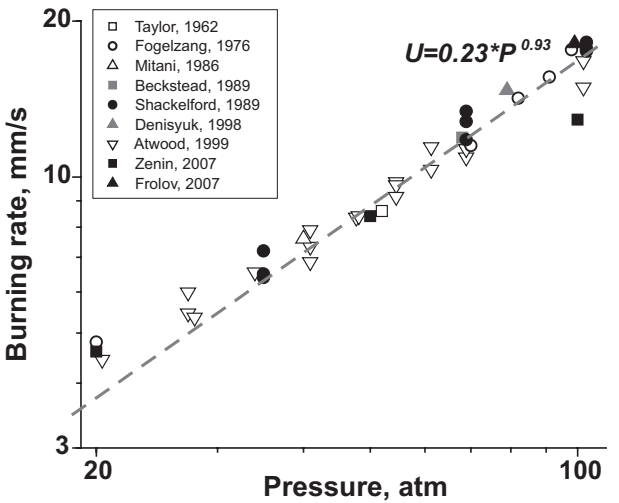
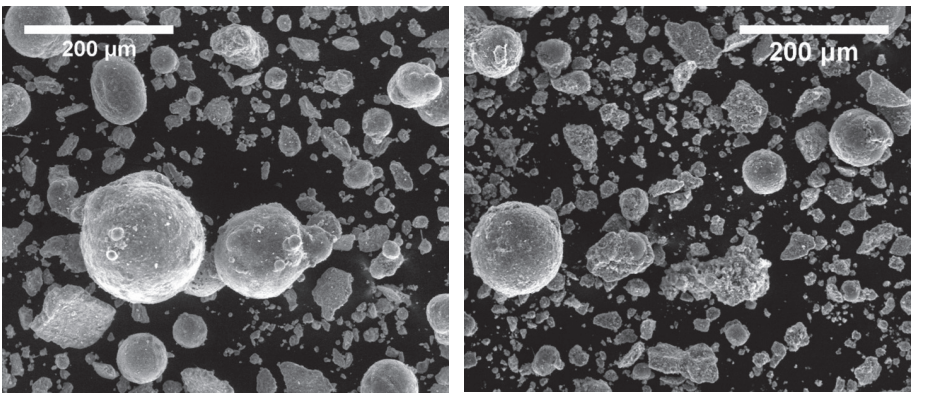



**Figure 10.** Comparison of obtained burning rate law (dashed line) with literature data.

The burning rate dependencies of binary compositions Al/HMX in the pressure range of 30-100 atm are presented in Figure 9b. Experiments reveal that composition with ultrafine aluminium and micro-sized HMX (uAl-mHMX) has a highest combustion velocity, which is about 25% higher than for composition with both ultrafine components, and approximately two times greater, than for samples where both of the components are micro-sized.

Burning rate of composition with micro-sized components is even smaller, than for HMX-monopropellant, and with pressure this difference is increasing, as illustrated in Figure 9b. The reason of this effect could be the spatial localization of the maximum energy-release zone of HMX (the sum of a stand-off distance and a flame thickness, d*) and a distance from the surface where the micro-sized aluminium particles burn out ($d_{al}$). Obviously, the micro-sized aluminium burns out at distance $d_{al} > d^*$, which results in burning rate decreasing of mAl-mHMX comparing to HMX monopropellant. With pressure d* value drops faster than $d_{al}$, leading to the pressure exponent decreasing comparing to monopropellant case.

**Combustion Residue**. Combustion residue was collected during combustion under nitrogen pressure 60 atm from the distance from the burning surface of 23 mm. Analysis of the combustion residue from the burning surface of the binary compositions with ultrafine aluminium and two types of HMX did not show any significant difference in the products morphology, as illustrated in Figure 11. Both powders contain at least two modes of the particle size – one in the range of tens micrometers, and another one – in a submicron range. Applying the comparative thermal analysis technique (specially elaborated to study the composition of aluminium agglomerates) we have detected the amount of unburnt aluminium in both cases: uAl-mHMX – 5%; uAl-uHMX – 5.0%; mAl-mHMX – 20.6%.




a) b)

**Figure 11.** SEM images of agglomerates: a) uAl-mHMX; b) uAl-uHMX.

**Mixing Technology**. "Green" mixtures to be compacted by pressing to fabricate samples for combustion experiments were prepared by two mixing techniques, *i.e.*, "dry" mixing and "wet" mixing with the use of ultra-sonic probe. Burning rates under initial nitrogen pressure 60 atm are compared in Figure 12. Application of "wet" mixing results in about 18% burning rate increase, comparing to "dry" technique. As it was shown, no fragmentation occurs during mixing; therefore such a rise could be attributed to a better shuffle of the particles.

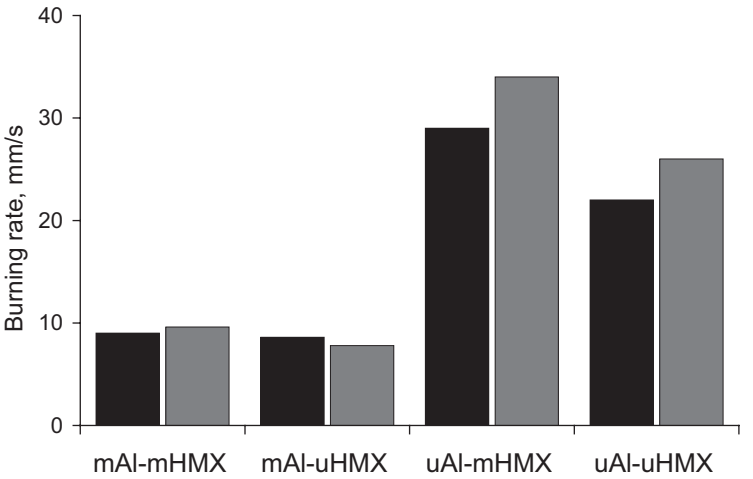



**Figure 12.** Influence of mixing type on burning rate for Al/HMX compositions: "dry" (black bars) and "wet" (grey bars) mixing.

However, even for the "wet" mixing the burning rate of composition with ultrafine components does not exceeds burning rate for formulation with micro-sized HMX and ultrafine aluminium. For micro-sized components "wet" mixing also increases combustion velocity, but not significantly (about 6%).

## Conclusion

Combustion parameters and morphology of compositions, based on aluminium and HMX, were studied at different component's particle sizes and different mixing techniques.

Morphology, dispersity and thermal behaviour for ultrafine and micro-sized aluminium and octogen were investigated. Obtained, average volume

diameter for ultrafine aluminium is 180 nm at chemical activity 84%, and for micro-sized one – 3.3 μm at 94.7%. Micro-sized HMX consists large crystals of about 100 μm, for ultrafine octogen the microstructure is more complicated and generally formed by particles about 200 nm. For ultrafine HMX the temperature peaks of the phase transformation and the thermal decomposition are shifted to the higher temperatures.

It was established, that burning rates of HMX monopropellants are almost identical for micro-sized and ultrafine octogen powders. Obtained U(P) values for micron-sized HMX are in a good agreement with the literature data.

Binary formulations of Al/HMX have been investigated with the particle size variation, containing ultrafine or micron-sized Al powders, and ultrafine or micron-sized HMX particles. For binary formulations with ultrafine aluminium a different spatial distribution of metal particles was found. Aluminium location is defined by HMX crystal sizes: for ultrafine octogen it is found to be much more uniform. The burning rate of formulations with ultrafine aluminium and micro-sized HMX is the highest.

It was shown, that "wet" mixing allows increasing combustion velocity at about 18% as compared to "dry" one, when ultrafine aluminium is used.

**Acknowledgment**

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