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A Comparison of Properties of Aluminized Composite Propellants Containing HMX and FOX-7

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Abstract: Modern rocket propellants contain inter alia nitroamines (i.e. RDX, HMX). Therefore, the detonation properties of composite solid propellants are very important for good functioning of rocket motors and for storage. One of the new materials of that kind, with low sensitivity, is FOX-7 which was applied here as one of the components of composite solid propellant. This paper presents the thermodynamical calculations and thermochemical research results as well as the results of a study of transition into detonation of an aluminized composite propellant containing HMX. The said properties were compared with those of a propellant containing FOX-7.

Keywords: detonation transition, HMX, FOX-7, aluminized composite propellant

Introduction

Over the last years, we can observe intensive activity in the development of new energetic materials for military applications. FOX-7 (1,1-diamino-2,2-dinitroethene, DADNE, $C_2H_4N_4O_4$) is one of the prominently interesting new materials of this kind. It is currently considered a very promising explosive material. 1,1-Diamino-2,2-dinitroethene is characterized by low sensitivity to initiating stimuli, high stability, contact compatibility with the standard components of modern explosive compositions and high detonation parameters [1-5]. FOX-7 has parameters comparable to RDX (hexogen, 1,3,5-trinitroperhydro-1,3,5-triazine, $C_3H_6N_6O_6$) and HMX (octogen, 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane,

$C_4H_8N_8O_8$) except that it is less sensitive. Therefore, FOX-7 can be successfully substituted for those materials in different kinds of compositions, also for RDX or HMX in the composite solid propellants which contain them [3].

This paper presents the thermodynamic calculations and results of research into an aluminized composite propellant containing HMX and a comparison of the results with those of a propellant containing FOX-7.

Experimental

Preparation of propellant samples

Propellant samples were prepared using a slurry cast technique. All solid ingredients were stored in water-jacketed ovens at 348 K to minimize the absorption of moisture from the atmosphere. Prior to incorporation into the mixture, the PBAN prepolymer was degassed overnight at 348 K in a vacuum drying oven.

The propellant was prepared in a vertical, 1.5-liter planetary action mixer at 348 K under reduced pressure. After the mixing cycle, the propellant was cast under vacuum into PVC tubes with an external diameter of 40 mm and an internal diameter of 37.5 mm. The propellant slurry was then cured at 348 K for two days in a water-jacketed oven.

The composition of the studied composite solid propellants (1 and 2) is shown in Table 1.

Granulometric analysis

The grain size distribution of the Al, AP, HMX and FOX-7 crystals was determined with the IPS-U (Infrared Particle Size) analyzer, version 8.12. The working principle of the IPS analyzer consists in the measurement of the variations of the IR beam which is dispersed by the particles moving within the measurement zone.

Trimodal AP is used as an oxidizer (small sized and large sized). The content of the small sized (fine-grained) AP in the propellant was 15%. Particle diameters of the fine-grained AP were below 50 μm. Particle diameters of the large sized (two fraction) AP were below 160 and 480 μm (Figure 1). Particle diameters of FOX-7 were below 560 μm and those of HMX were below 180 μm. Particle diameters of aluminum powder (Al) were below 60 μm (Figure 1).

Table 1. Composition (wt. %) of the propellant formulations

Components	Propellants	
	1	2
AP	50.00	50.00
PBAN/Epoxide	16.61	16.61
Al	5.00	5.00
DOA	6.39	6.39
HMX	22.00	0.00
FOX-7	0.00	22.00

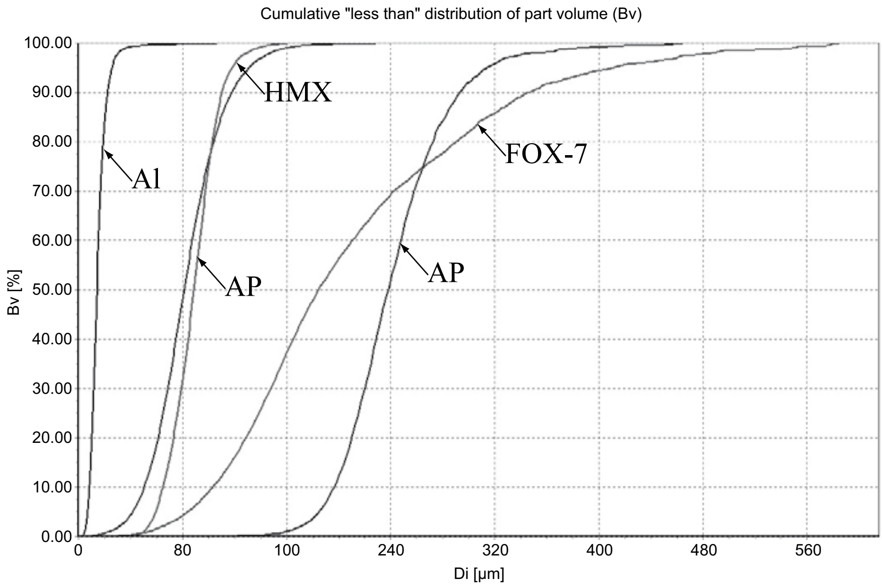


Figure 1. Cumulative distribution of the volume of Al particles, AP (two fractions), HMX and FOX-7.

Thermal analysis

A differential thermal analysis was made using a DTA 551 Ex apparatus manufactured by OZM Research. The analysis were performed by heating a 30 mg sample at a rate of 10 K/min in the presence of the static air. Analyses were performed in open test tubes. A thermocouple protected by a glass sheath was inserted directly into the sample. Data were evaluated using the MEAVY 2.0.0.4 software of DTA 551 Ex analyzer. The onset (T_{onset}) and the maximum (T_m) of the first exothermal effect were determined on thermograms (Figure 2).

The onset of decomposition peak (T_{onset}) and the maximum peak (T_m) of the propellants are presented in Table 2.

Heat of combustion

The combustion experiments were conducted in a stationary bomb calorimeter with automatic temperature measurement under reduced pressure ensuring minimum oxygen atmosphere (3.3 kPa pressure). The adiabatic bomb IKA C 4000 calorimeter system was used to determine the heat of combustion. The calorimeter was calibrated by burning standard propellant. The results of the heat of combustion study of the propellants are presented in Table 2.

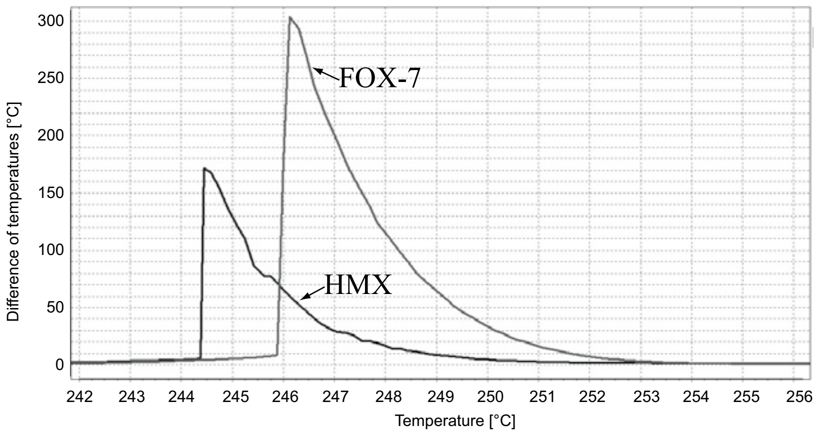


Figure 2. DTA thermograms of the propellants containing HMX and FOX-7.

Burning rate

The determination of the burning rate of the studied propellant samples under a pressure of 0.1 MPa and a temperature of 293 K (u_1, Table 2) was made by measuring the time of propagation of the burning reaction front over a specified section (5 mm) of the studied samples in the shape of cylinders burning frontally (with inhibited side surface). The EXPLOMET-FO-2000 apparatus was used to make this type of measurement (the apparatus employs a method based on the emission of light generated by the burning reaction front). The EXPLOMET measures the time intervals between the illumination of two consecutive probes and calculates the burning rate. The light signals that actuated the instrument and enabled measurement of the time intervals between the measuring bases were provided via an optical cable. The results are presented in Table 2.

Thermodynamic calculations

Thermodynamic calculations were carried out to predict the heat of explosion, explosion temperature and the volume of gases for the tested aluminized composite propellants (Table 1). The calculations were performed using ICT-Thermodynamic Code for V = const. The obtained results are presented in Table 2. The reaction products and their quantities are shown in Figures 3 and 4. The main reaction products of both propellants as follows: CO_2, H_2O, N_2, CO, H_2, HCl and Al_2O_3. The studied propellants are also characterized by the same volume of gas products while their temperature of explosion differs by about 150 K (Table 2).

Table 2. The characteristics of the propellant formulations, measured and calculated

Properties	Propellants	
	1	2
ρ, g·cm^{-3}	1.61	1.61
T_{onset}, K	517.3	518.9
T_m, K	517.6	519.3
u_1, burning rate (p = 0.1 MPa), mm s^{-1}	1.02	0.85
Heat of combustion (Q), kJ·kg^{-1}	4194	3900
Explosion temperature (T_{ex}), K	2804	2650
Heat of explosion (Q_{ex}), kJ·kg^{-1}	4262	4001
Heat of explosion (gaseous water) (Q_{exw}), kJ·kg^{-1}	4057	3796
Average heat of explosion ($Q_{aver} = (Q_{ex}+ Q_{exw})/2$), kJ·kg^{-1}	4160	3899
Gas volume including H_2O at 25 °C , cm^3 g^{-1}	904	904
Oxygen Balance (OB), %	-52.7	-52.7

Detonation transition

An electronic method using short-circuit (electrocontact) type sensors was applied to determine the detonation velocity. Two twisted copper wires were used, one of them insulated, the another not [6, 7]. In sensors of this type, the closure of the electric circuit is caused by the mechanical effect of the detonation wave pressure.

The cylindrical propellant charges (height [h] = 250 mm) prepared as described above (see preparation of propellant samples) were used in the experiments. Detonation velocity was determined for three measuring bases by applying four fusion sensors. A TM 1107 microseconds timer was used for time measurements. An HT-14 booster (14 g of RDX/TNT mixture, d = 20 mm, L = 25 mm) was used to initiate detonation. The velocity measurement accuracy was about 1%.

A diagram of the detonation velocity measuring system is presented in Figure 5 (L_0 = 80 mm, L_1 = L_2 = L_3 = 50 mm). The detonation velocity was calculated with equation (1):

$$V_{det} = L/t \tag{1}$$

where L is the distance between sensors while t is the time of passage of the detonation wave between sensors. The detonation velocity determined for the propellant containing HMX was $[V_{det}] = 4669$ m s^{-1}.

In Figure 6a, a photograph of the steel plate (see Figure 5) after detonation of propellant charge containing HMX is presented. Figure 6b presents a photograph of the plate used in the experiment with the propellant containing FOX-7. Obviously, this charge did not detonate. Their undetonated fragments are shown in Figure 7.

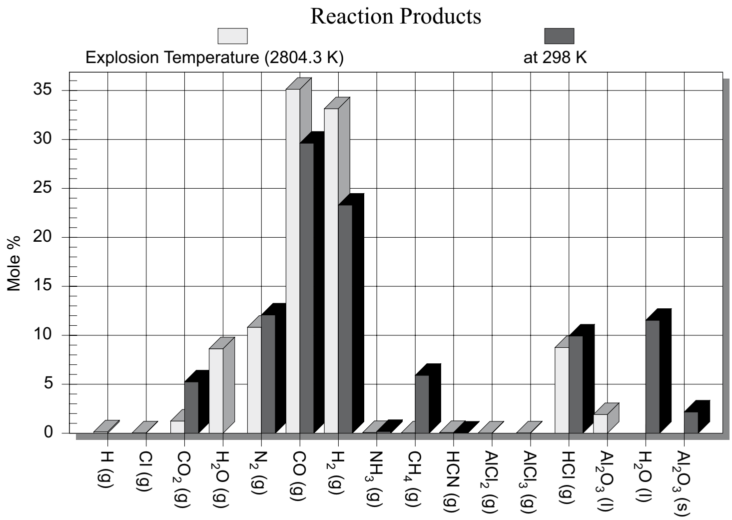


Figure 3. Graphical representation of the calculated reaction products of the tested composite solid propellant containing HMX.

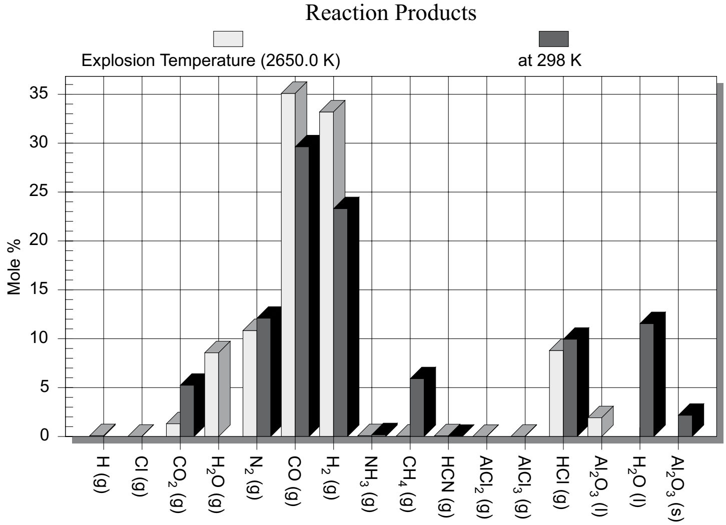


Figure 4. Graphical representation of the calculated reaction products of the tested propellant containing FOX-7.

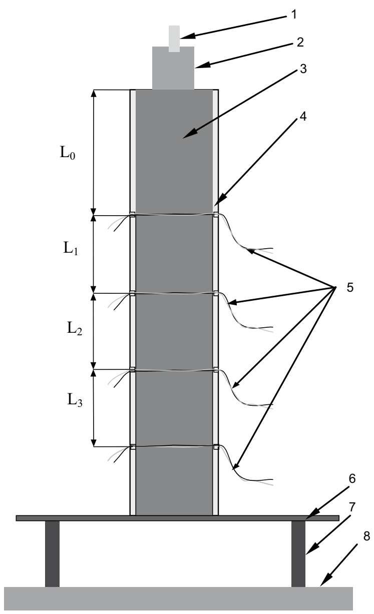
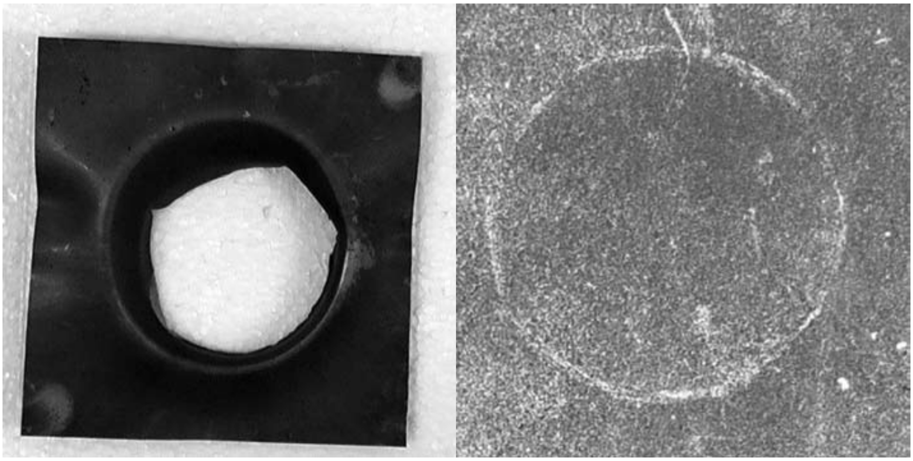


Figure 5. Diagram of the system used for the determination of detonation velocity: 1 – detonator, 2 – booster, 3 – propellant charge, 4 – PVC tube, 5 – short-circuit sensors , 6 – steel plate, 7 – steel cylinder, 8 – ground base.



a) b)

Figure 6. The witness steel plates: (a) after detonation of HMX-containing propellant charge (b) steel plate used in the experiment with FOX-7 containing propellant charge.

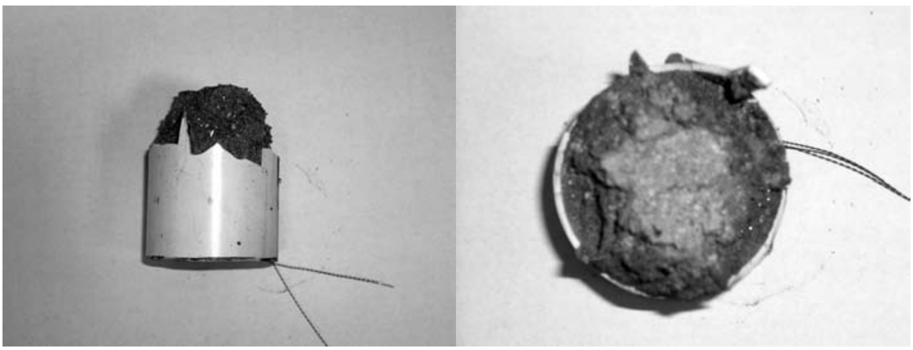


Figure 7. Undetonated fragments of the propellant charge containing FOX-7.

Conclusions

On the basis of the conducted investigations and the results obtained, we can formulate the following conclusions:

1. The propellant containing 22% of FOX-7 has a comparable deflagration temperature and the same volume of gaseous reaction products as the composite propellant containing 22% of HMX.
2. The linear combustion velocity u_l of the tested propellant containing FOX-7

is approximately 17% less than that of the propellant containing HMX

3. The measured heat of combustion of each propellant is comparable to the average heat of explosion calculated for those propellants.
4. Preliminary investigations have shown that the composite propellant containing 22% FOX-7 does not detonate when boosted with HT 14.

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