

## Effect of the Addition of Ultrafine Aluminum Powders on the Rheological Properties and Burning Rate of Energetic Condensed Systems

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The effect of small additives (1.25–5.00%) of ultrafine aluminum powders (UFAP) on the rheology and combustion of model four-component energetic condensed systems is studied. It is found that the addition of UFAP decreases the temperature of HMX decomposition. Small additives of UFAP increase the burning rate of model energetic condensed systems and decrease the exponent  $\nu$  in the burning rate law without deteriorating the rheological characteristics of the model propellants.

**Key words:** ultrafine aluminum powders, energetic condensed systems, passivation, HMX, ammonium perchlorate, rheology, burning rate.

### INTRODUCTION

One method of increasing the burning rate of aluminized energetic condensed systems [1] is to reduce the Al particle size [2]. Theoretically, the Al particle size can be reduced to the sizes of separate atoms and clusters but powders are difficult to produce from such particles: in contact, the particles sinter at temperatures below room temperature [3]. It is more expedient to produce stabilized Al powders with a surface-averaged particle size less than 0.5  $\mu\text{m}$  [ultrafine aluminum powders (UFAP)] [4–6]. It is known that UFAPs produced by electrical explosion improve the combustion characteristics of energetics systems [7]. Experiments have shown that the use of UFAPs instead of commercial powders (surface-averaged particle size  $\approx 10 \mu\text{m}$ ) can lead to a twofold increase in the burning rate of energetic condensed systems containing 55% nitrocellulose (NC) (13.5% N), 30% dioxethylnitramine, and 15% Al [8]. It has been shown [5, 6] that the complete replacement of commercial powders by UFAPs results in an increase in the burning rate of systems based of

an active rubber binder (20%), ammonium perchlorate (AP) (27%), HMX (35%), and Al (18%). In some cases, the exponent  $\nu$  in the burning rate equation  $u = Ap^\nu$  decreases, the completeness of metal combustion increases, and the degree of agglomeration decreases, but the cast properties of energetic materials are deteriorated by the addition of UFAP [9]. The purpose of the present work is an integrated study of the ballistic characteristics and rheology of propellants containing UFAPs in the case of partial replacement of the metal fuel by an UFAP.

### EXPERIMENTAL RESULTS AND DISCUSSION

In the present study, the rheology and burning rate law of a model four-component mixture for various types of UFAPs produced by electrical explosion in gaseous argon [10]. Along with UFAPs, whose particles are coated with an oxide shell (UFAP– $\text{Al}_2\text{O}_3$ ), we studied powders passivated by  $\text{AlB}_2$  (UFAP– $\text{AlB}_2$ ) and NC (UFAP–NC). The passivating  $\text{AlB}_2$  coating was applied to enhance the oxidation stability of the particles and reduce aluminum particle agglomeration during the production process [10]. The specific surface area ( $S_{\text{sp}}$ )

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TABLE 1

Characteristics of Aluminum Powders

Type of powder	$S_{sp}$ , m <sup>2</sup> /g	$a_s$ , μm	$C_{Al}$ , %
ASD-4	0.4	5.6	98.5
UFAP-Al <sub>2</sub> O <sub>3</sub>	7.0	0.3	76.0
UFAP-AlB <sub>2</sub>	17.0	0.1	78.0
UFAP-NC	5.0	0.4	68.0

**Notes.** The quantities  $S_{sp}$  and  $C_{Al}$  were determined by the Brunauer–Emmet–Teller (BET) method and volumetric method (from the volume of hydrogen released by the reaction with a 10% solution of NaOH), respectively;  $a_s$  is the surface-averaged particle diameter ( $a_s = 6/S_{sp} \cdot 2.7$  for spherical aluminum particles).

of the powder coated with AlB<sub>2</sub> is  $\approx 2.5$  times larger than that of a powder with an oxide shell (Table 1). An NC coating was applied to study the activation of aluminum oxidation due to the high exothermic effect of NC decomposition at a temperature of 180°C. To produce an NC coating containing 12.4% nitrogen, an UFAP was treated by a 10% solution of NC in acetone with the subsequent vaporization of acetone at room temperature. As a result, the UFAP contained 33% NC and retained flowability.

The model mixture consisted of AP, HMX, Al (25%), and an inert binder based on SKD-1 rubber. The metal fuel was an ASD-4–UFAP mixture (25%) in which the mass content of UFAP was 1.25–10% of the total mass of the mixture.

The components of the energetic condensed system were investigated by differential thermal analysis (DTA). The DTA results are given in Fig. 1. The temperature of the beginning of intense oxidation and the degrees of oxidation of the examined aluminum powders depend on the particle size of the powders. The degree of oxidation  $\alpha$  (or the specific degree of conversion of metallic aluminum in the starting powder to aluminum oxide) is calculated by the formula

$$\alpha_{Al \rightarrow Al_2O_3} = \frac{+\Delta m}{C_{Al} \cdot 0.89} \cdot 100\%. \quad (1)$$

Here  $+\Delta m$  is the mass gain (%) observed on the thermogravimetric (TG) curve, and  $C_{Al}$  is the mass content of metallic aluminum (%) in the starting UFAP (see Table 1).

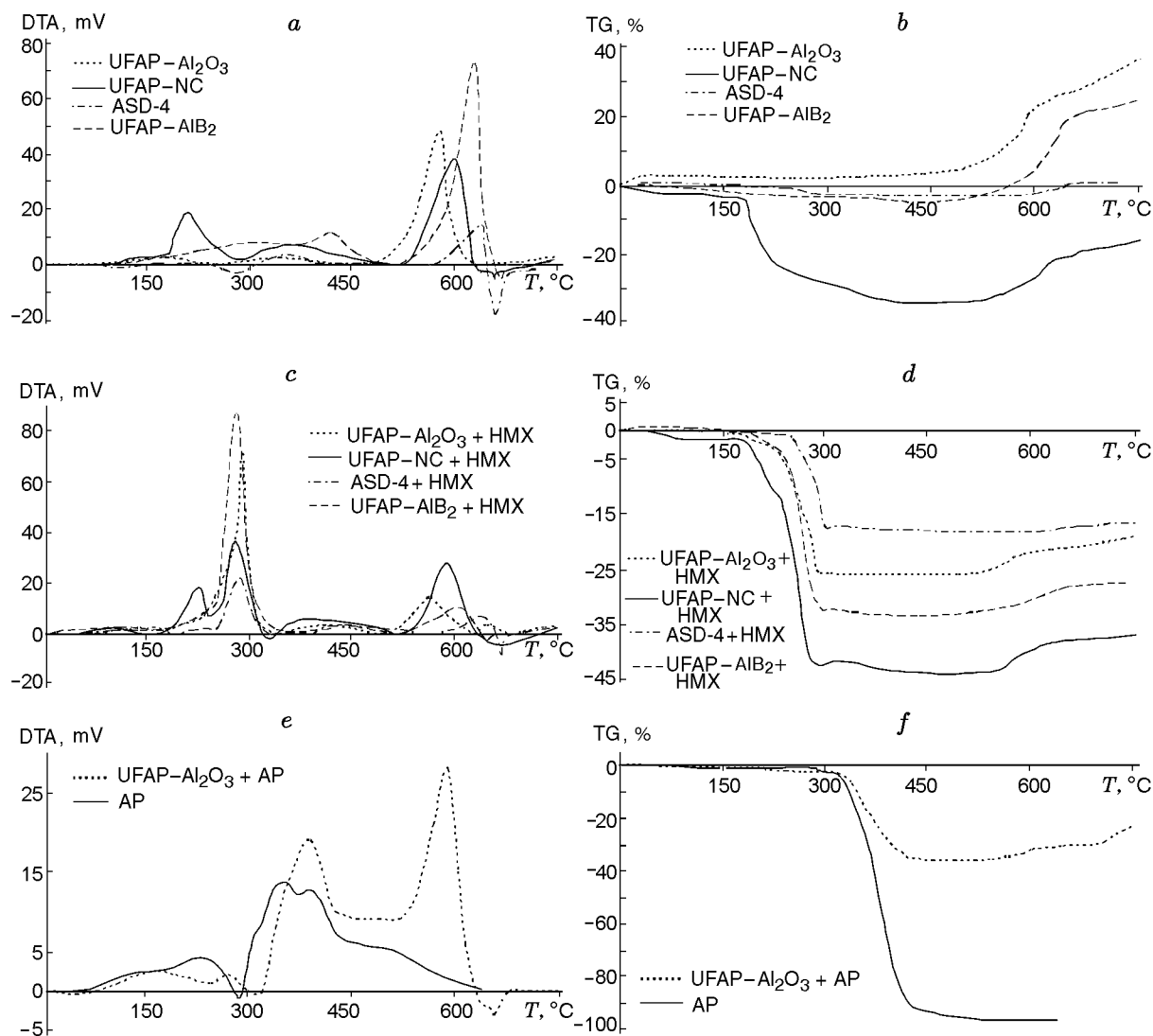
For the ASD-4 commercial powder, the temperature of the beginning of intense oxidation is 600°C, and for the UFAP coated with Al<sub>2</sub>O<sub>3</sub>, it is 510°C (Fig. 1a). Thus, the degree of oxidation of UFAP–Al<sub>2</sub>O<sub>3</sub> ( $\alpha = 28.3\%$  to  $T = 660^\circ\text{C}$ ) is much higher than that of the ASD-4 powder ( $\alpha = 1.8\%$ ) (Fig. 1b). The tempera-

ture of the beginning of intense oxidation of the UFAP with an AlB<sub>2</sub> coating (560°C) is higher than that of UFAP–Al<sub>2</sub>O<sub>3</sub> (510°C). This is likely due to the protective action of the high-melting AlB<sub>2</sub> film. In this case, the degrees of oxidation of UFAP–Al<sub>2</sub>O<sub>3</sub> and UFAP–AlB<sub>2</sub> at temperatures above 660°C are approximately identical. The temperature dependence of the DTA signal for linear heating of UFAP–NC has two exothermic effects due to NC decomposition at temperatures of 180–280°C with a 25% mass loss and oxidation of metallic Al (510–620°C). At temperatures of 280–510°C, the most probable process is the gasification of the carbon residue formed by NC decomposition. The total mass loss due to NC decomposition (on the TG curves) is 31.2%. Intense aluminum oxidation for UFAP–NC occurs at  $T = 525\text{--}620^\circ\text{C}$ ; in this case,  $\alpha = 19.4\%$ . As follows from the DTA results, the transformations of NC and UFAP under heating in air proceed independently of each other. The thermal-decomposition parameters of NC and the oxidation parameters of UFAP remain at the level of the characteristics of thermal decomposition of the individual substances.

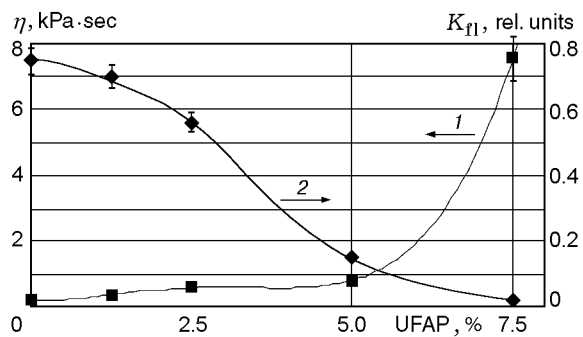
The DTA results for UFAP–Al<sub>2</sub>O<sub>3</sub> + 50% HMX mixtures show that intense decomposition of HMX in the mixture begins at a temperature of 260°C (Fig. 1c), which is 20°C lower than that for HMX without the additives (280°C). Thus, UFAP–Al<sub>2</sub>O<sub>3</sub> initiates HMX decomposition at a lower temperature. The presence of HMX does not change the oxidation parameters of UFAP–Al<sub>2</sub>O<sub>3</sub>. UFAPs coated with AlB<sub>2</sub> and NC have a similar effect on the temperature of the beginning of intense decomposition of HMX, i.e., they decrease it to 240 and 250°C respectively. The DTA curve of the ASD-4 + 50% HMX mixture also shows a decrease in the temperature of the beginning of intense decomposition of HMX (to 270°C). For ASD-4 in a mixture with HMX at a temperature of up to 660°C the degree of oxidation is  $\alpha = 1.1\%$ , which is much lower than the degree of oxidation of the UFAP–Al<sub>2</sub>O<sub>3</sub> sample, for which  $\alpha = 13.3\%$  at 660°C (Fig. 1d).

In the UFAP–Al<sub>2</sub>O<sub>3</sub> + 50% AP mixture, the decomposition parameters of AP remain almost unchanged. The oxidation of UFAP–Al<sub>2</sub>O<sub>3</sub> in the mixture with AP begins at 480°C, which is 30°C lower than that of UFAP–Al<sub>2</sub>O<sub>3</sub> without AP (Fig. 1e and f).

The mixing procedure for the components of the energetic condensed system included thermostatic control and evacuation operations. The viscosity of the compositions was determined on a Geppler viscosimeter [11]. The fluidity coefficient ( $K_f$ ) of the propellant mass was determined by a standard procedure [12]. The variation of the rheological characteristics of the compositions is shown in Fig. 2. At a mass concentration



**Fig. 1.** DTA and TG curves for linear heating of the model-mixture components in air (a sample mass of 40 mg, a heating rate of 10 K/min, and  $\alpha$ - $\text{Al}_2\text{O}_3$ ) as the reference material.



**Fig. 2.** Structural viscosity (curve 1) and fluidity factor (curve 2) of the model mixture versus the content of  $\text{UFAP-Al}_2\text{O}_3$  with the replacement of the ASD-4 commercial powder in the model energetic condensed system.

of  $\text{UFAP-Al}_2\text{O}_3$  less than 5%, the structural viscosity ( $\eta$ ) of the composition (curve 1 in Fig. 2) increases slowly, and then at a 7.5% content of  $\text{UFAP-Al}_2\text{O}_3$ , it increases sharply. At the same time, the fluidity coefficient (curve 2 in Fig. 2) decreases smoothly as the  $\text{UFAP-Al}_2\text{O}_3$  content increases to 5%. In this case, the mass completely loses fluidity; therefore, in the manufacture of propellant samples for combustion, the  $\text{UFAP}$  content in the energetic condensed systems was limited by a level of 5%. For combustion, we used uncured cylindrical samples 7 mm high and 10 mm in diameter, reinforced by fabric-based laminate on the lateral surface. The samples were kept at 60°C for 30 min and evacuated at a residual pressure of 10 kPa for 10 min.

TABLE 2

Effectiveness of the Exponent  $\nu$   
in the Combustion Law of the Model Energetic Condensed Systems

No.	Content (type) of UFAP in the system, %	K at a pressure		Burning rate law
		4.0 MPa	20.0 MPa	
1	0	1.0	1.0	$u = 3.3p^{0.50}$
2	1.25 (UFAP–Al <sub>2</sub> O <sub>3</sub> )	1.2	1.0	$u = 4.5p^{0.39}$
3	5.00 (UFAP–Al <sub>2</sub> O <sub>3</sub> )	3.6	2.3	$u = 16.8p^{0.23}$
4	2.50 (UFAP–AlB <sub>2</sub> )	1.1	1.0	$u = 3.7p^{0.44}$
5	5.00 (UFAP–AlB <sub>2</sub> )	3.4	2.1	$u = 16.8p^{0.20}$
6	2.50 (UFAP–NC)	2.9	1.8	$u = 14.3p^{0.20}$

Combustion of the samples was conducted in a nitrogen atmosphere in a constant-pressure device [13]. The samples were fixed upright and ignited from the top with black powder. The pressure (LK412/250 pressure transducer) and the flame glow intensity (FD-3 photodiode) were recorded automatically during the combustion. The burning time of the samples was determined by a pressure–time dependence. The pressure increased during the experiment (on the average by 0.1 MPa), and the burning rate was therefore normalized by the average pressure value. Statistical processing of the results was performed with the Statistika software package. For the coefficients  $A$  and  $\nu$  in the burning rate law of the energetic condensed system, the relative measurement error was  $\pm 4.9$  and  $\pm 5.2\%$ , respectively, at a confidence probability of 0.95. The combustion characteristics in the pressure range of 4.0–20.0 MPa are presented in Table 2. The effect of UFAP additives on the burning rate of the samples was evaluated using the dimensionless coefficient

$$K = u/u_0 \quad (2)$$

at pressures of 4.0 and 20.0 MPa. Here  $u$  is the burning rate of the samples with UFAP, and  $u_0$  is the burning rate of the samples containing no UFAP.

As follows from Table 2, if ASD-4 is partially replaced by UFAP, the burning rate increases in accordance with the increase in the UFAP content. At UFAP contents of 1.25 and 5.0%, the burning rate at a pressure of 4.0 MPa increases by a factor of 1.2 and 3.6. The exponent  $\nu$  decreases from 0.5 (the sample containing no UFAP) to 0.39 and 0.23. The increase in the burning rate of the energetic condensed system due to the partial replacement of ASD-4 by UFAP is apparently explained by the smaller combustion time of UFAP particles.

One more factor responsible for the increase in the burning rate upon the addition of UFAP is a decrease

in the degree of particle agglomeration in the combustion wave with increasing particle size of aluminum. It has been shown previously [14] that the higher the aluminum particle size, the smaller the volume-averaged size of the agglomerates formed. The surface area of the agglomerated particles remains large enough, so that their higher burning rate is higher than the burning rate of large particles of ASD-4 even under the agglomeration conditions of the UFAP combustion products.

The decrease in the exponent  $\nu$  due to the addition of UFAP can be related to the effect of UFAP on the heat release in the condensed-phase reaction layer. The thermal contribution from aluminum oxidation in the condensed-phase reaction layer increases as the aluminum powder content increases and as the initial particle size decreases [15]. The fraction of the heat released in the condensed phase as a result of aluminum oxidation ( $d = 20\text{--}60\ \mu\text{m}$ ) is  $\approx 25\%$  of the total amount of heat released in the condensed phase [15]. Because the reactivity of UFAP is higher than that of ASD-4, one might expect a higher temperature in the UFAP oxidation zone and an enlargement of the heating zone of the condensed phase. The temperature increase and the enlargement of the heating zone apparently result in a reduction in the role of the processes occurring in the aerosol zone and a decrease in the coefficient  $\nu$  for the UFAP-containing compositions. A considerable increase in the particle size of the UFAP–AlB<sub>2</sub> sample did not lead to an increase in the burning rate of the model energetic condensed system compared to the composition containing UFAP–Al<sub>2</sub>O<sub>3</sub> (see Table 2). It is probable that during mixing of UFAP and rubber, the UFAP–Al<sub>2</sub>O<sub>3</sub> particle agglomerates disintegrated and the stronger agglomerates in the system containing UFAP–AlB<sub>2</sub> sintered in the heating zone with a particle size reduction. The addition of 2.5% UFAP–NC to

the system resulted in the same increase in the burning rate and the same decrease in the exponent  $\nu$  as with the addition of 5% UFAP–Al<sub>2</sub>O<sub>3</sub>. In the UFAP–NC sample, the mass concentration of NC was 33%; therefore, on propellant basis, the UFAP content was 1.7% and the NC content was 0.8%. NC is characterized by a low temperature of the beginning of intense decomposition (160°C); therefore, there is a high probability that NC undergoes an exothermic decomposition in the condensed-phase reaction layer. Because of the low content of NC in the propellant, the heat release in the thermal decomposition of NC is insignificant and cannot have an appreciable effect on the heat balance of the condensed phase since NC reacts weakly with UFAP. Apparently, the reason for the effectiveness of NC as a modifying agent of combustion is its interaction with the other propellant components, in particular, with AP.

## CONCLUSIONS

DTA results showed that the addition of UFAPs reduces the decomposition temperature of HMX and did not affect the decomposition temperature of AP. Small additives of UFAPs (2.5 and 5%) increased the burning rate by a factor of 1.2 and 3.6 (at a pressure of 4.0 MPa), respectively, and reduced the exponent  $\nu$  in the burning rate law from 0.5 (propellant containing no UFAP) to 0.39 and 0.23, respectively. The UFAP coated with NC was found to be a highly effective modifying agent for combustion of the propellants studied. The addition of 2.5% UFAP coated with NC to the propellant studied increased the burning rate by a factor of 2.9 at a pressure of 4.0 MPa (compared to the starting composition based on ASD-4) and decreased the exponent  $\nu$  to 0.20. The addition of small amounts of UFAPs to metallic fuels can be used as a method for decreasing  $\nu$  for energetic materials containing aluminum.

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