EFFECT OF ORGANIC COATINGS OF NANOALUMINUM ON THE BURNING RATE OF MIXED COMPOSITIONS

by

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Mixed compositions based on ammonium perchlorate, inert fuel-binder and nanosized aluminum, encapsulated with organic compounds, have been experimentally studied. The study of aluminum powders using scanning electron microscopy and transmission electron microscopy was carried out. The oxidation of aluminum powders was investigated by differential thermal and thermogravimetric methods. The chemical composition of the condensed products was determined by X-ray diffraction. The laws of mixed composition combustion were determined in a wide pressure range. The possibility of controlling the burning rate and the content of condensed combustion products by using encapsulated nanoaluminum is shown.

Keywords: *nanosized aluminum powder, burning rate*
mixed compositions, organic coatings,
condensed products of combustion

Introduction

The main components of mixed compositions (MC) used in gas generators for wide application are an oxidizer and an organic fuel-binder. Metal powders, for example, aluminum, magnesium, zirconium, and other metals and alloys, are employed as additives to the fuel-binder. As far as metal powders are concerned, aluminum is of greatest interest as a consequence of the low melting temperature of pure aluminum and its oxide (in comparison with magnesium, zirconium, and beryllium), its availability, acceptable cost, and high heat release when burned with oxygen [1]. In [2-6] it was shown that the introduction of aluminum nanopowder (nAl) into the makeup of solid MC makes it possible to significantly increase the burning rate, decrease the ignition delay time, increase the completeness of aluminum combustion, and decrease the loss of specific impulse.

Application of nAl allows creating high-energy materials with new properties [7, 8]. During storage and processing of nanopowders there are several problems associated with the aggregation of powders and their high chemical activity. To reduce the activity nAl are being passivated by air oxygen, thereby a thin oxide film with a thickness of 2-8 nm is forming [9]. Oxide film prevents further oxidation of aluminum. At the same time, there is a decrease in

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the content of pure metal in nAl ($C_{Al} < 95\%$ by mass). To increase the reactivity of metallic fuel is possible by increasing the stability of metal nanopowder particles to oxidation and by reducing of particle agglomeration during the production and storage. In this regard, studies are being conducted to improve the quality of passivation by searching for effective passivating reagents and increasing the content of metallic aluminum in the particle.

Nowadays different methods for increasing nAl reactivity are known. One method is the modification of nAl particles by it encapsulating with organic compounds. Recently there were published series of articles discussed the study of nAl coated with fluoropolymer Viton, stearic acid and other organic compounds [9, 10]. The advantages of *non-oxide passivation* are the higher calorific value of powders coated with organic passivating layers, and good adhesion of such coatings with fuel-binder. The study of the effect of encapsulated nanoaluminum powders on combustion characteristics of MC is of particular interest.

The aim of this work is to study the effects of different types of organic coatings on burning properties of nanosized aluminum powder and solids content of the combustion products of high- energy mixed composition in a wide pressures range.

Experimental technique

Investigations were carried out on MC containing ammonium perchlorate (AP) and the inert fuel-binder SKDM-80 in the pressure range from 0.04 to 6.0 MPa. There were used two fractions of AP: <50 microns – in the study of combustion at pressures 1-6 MPa and 165-315 microns at pressures 0.04-0.08 MPa. As a metal fuel three types of powders were used:

- standard nano-sized aluminum powder Alex brand (type A1),
- Alex, coated with a fluoropolymer Viton (A2), and
- Alex, coated with heterocyclic organic compound 8-hydroxyquinoline (A3).

Components of MC were thoroughly mixed by hand, and then cylindrical samples armored on the lateral surface were prepared. To ensure the results reproducibility the density scatter for all selected samples did not exceed 0.02 g/cm^3. Other conditions were being constant: excess oxidant ratio $\alpha = 0.5$ and aluminum powder content 15 wt.%.

A study of aluminum powders by SEM (Philips CM 12) and TEM (Quanta 200 3-D) were done. Study of aluminum powders oxidation were done by heating in air by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The differential scanning calorimetry (DSC)/TGA analyses were carried out using a NETZSCH STA 409 PC/PG set up. Powders (6-7 mg) were heated up to 1000 °C at 10 °C per minute under an air flux of 190 mL per minute.

Determination of stationary burning rate at pressure $p > 0.1$ MPa was carried out on a constant pressure device and at subatmospheric pressures – vacuum chamber was used [11]. At each data point 3-7 replicates were held. Statistical analysis was performed using the standard MathCad program pack on the assumption that the distribution of random errors of measurement results is normal (Gaussian). The relative error of measurement of the burning rate at a confidence level of 0.95 did not exceed 5-7%.

Determination of the condensed combustion products content, z, was carried out at atmospheric pressure by burning samples outdoors. Value z was determined as the ratio of condensed particle mass deposited in a quartz sorter to the mass of the original sample. Relative error in determining the solids content does not exceed 1.5%. The chemical composition of condensed combustion products, crystal structures and their volumetric content were determined by X-ray diffraction.

All mentioned TEM, SEM, DTA, DSC, TGA, XRD research methods are actively used by various researchers [12, 13] to determine particle size, shape, surface area, morphological data, reactivity parameters of metal powders, *etc.*

Results and discussion

The SEM provides information about the external (visible) particle shape and size, but not its structure. Analysis of the study results showed a significant influence of the nature of organic coating of Alex powder on the condensed product morphology.

During the study there was found difficulty of metal particle separating in sample preparation in the case of the standard (uncoated) Alex powder and near impossibility to separate (by standard methods) Alex powder particles, coated with a fluoropolymer.

Micrograph, fig. 1, clearly shows that the shape of the particles of standard uncoated Alex powder is spherical. Alex powder aggregates formed from particles of 50-100 nm in diameter and more. Micrograph of aluminum powder type A2, fig. 2, is an agglomerated mass of particles and even at high magnification individual particles cannot be seen, as the particles are sufficiently tightly adjacent to each other.

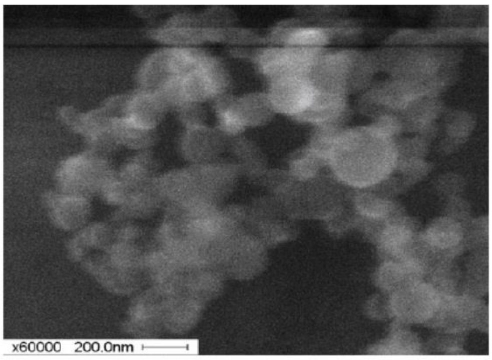

Figure 1. Micrograph of aluminum powder type A1

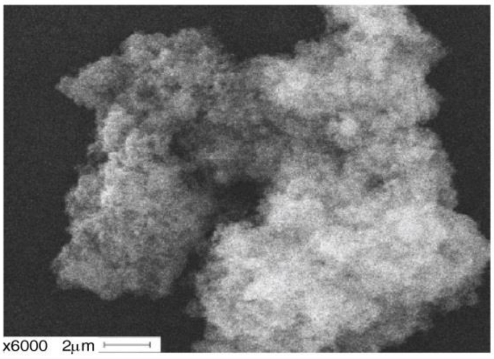

Figure 2. Micrograph of aluminum powder type A2

Thermogravimetric (TG) and DSC analysis methods shows that the aluminum powder type A2 burning process consists of three stages, fig. 3.

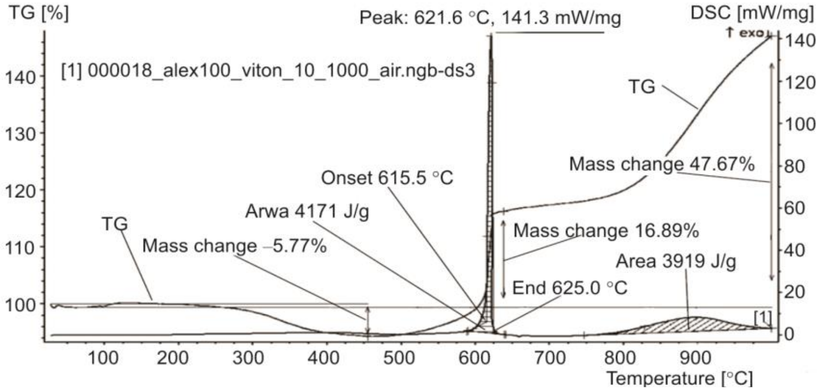

Figure 3. Derivation of aluminum powder type A2

At the first stage, the weight loss of the testing substance is observed that is obviously due to the decomposition of organic matter of the coating. The initial mass loss for this sample is higher than for the powder type A1. The second stage of low temperature oxidation of the aluminum powder type A2 proceeds at a high rate in the temperature range of 500-625 °C, and there is the lowest value of total heat release. The value of the peak of the heat effect is 4 times greater than that of type A1 (uncoated) aluminum powder. The sample type A2 also features the lowest mass increase at the end of the second phase of oxidation. Thus, it can be assumed that the fluoropolymer coating performs a protective action for particles of nAl. This property can be interesting in the perspective of using of nAl as energetic additive, because it might improve aging characteristics of the powders. The third stage is connected with the high temperature oxidation of the metal, it starts at a temperatures of about 800 °C, as a result of oxygen diffusion acceleration to the metal particles at high temperature.

The derivation of aluminum powder type A1 is shown in fig. 4.

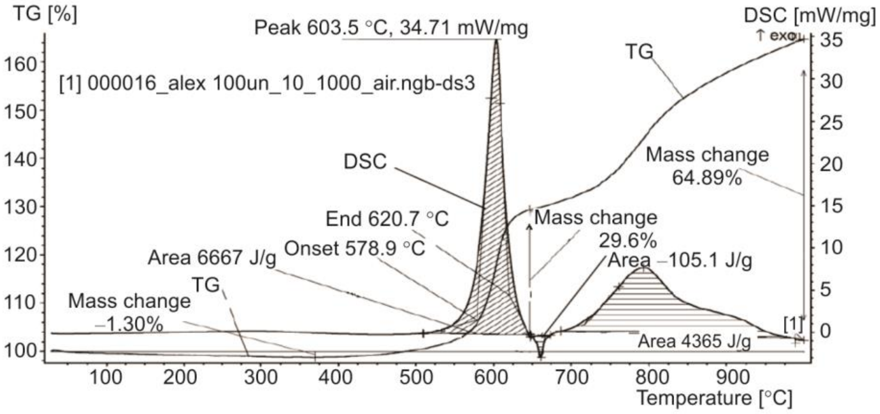

Figure 4. Derivation of aluminum powder type A1

The main experiment to measure the steady-state burning rate was carried out at atmospheric pressure in the open air. In the MC, based on AP of dispersion 165-315 microns and containing coated aluminum A3, the burning rate, with respect to the base system with aluminum A1, increases in 26%. It should be noted that value of z in A3 composition is reduced by 19%.

The A2 composition based on the coarse AP burns steadily, but the burning rate in comparison to the basic composition A1 is reduced by 7%, while z increases by 29%. This effect of A1 coating on the burning rate correlates with the thermal analysis data, figs. 3 and 4, which indicates that initial oxidation temperature of aluminum coated with fluoro-organic polymer is higher than initial oxidation temperature of *Alex*. It can be assumed, that the MC, regardless of the AP dispersion and containing aluminum powder coated with fluoropolymer can work efficiently at high temperatures and pressure range $p > 0.1$ MPa. Point experiment shows that the samples based on fine AP and aluminum powder coated A2 for $p = 1$ MPa have a burning rate of 7.6 mm/s.

Analysis of experimental results, carried out at atmospheric pressure, showed that the selection of an effective coating for nAl, as well as the possibility of AP encapsulation with organic compounds can provide not only high power performances of MC but also facilitate the manufacturing techniques for such compositions. Analysis of the results of MC combustion in a wide pressures range showed the influence of the type of coating on the burning rate and the exponent ν in the burning rate law $u = u_0p^\nu$, as well as the impact on the amount of condensed combustion products, see tab. 1. Note that at high pressures the level of burning rate and the amount of condensed combustion products of MC containing aluminum powder A2 is higher compared to compositions containing aluminum A3. Nevertheless the MC containing aluminum powder A2 type show lowering in pressure sensitivity.

Table 1. Effect of aluminum coatings on the combustion characteristics

Types of metal fuel	Burning rate law, *u*, [mms^{-1}]	Pressure range, [MPa]	*z*, [wt.%]
A1	$u = 1.5$	0.1	10.0
A2	$1.53\,p^{0.73}$	0.04-0.08	-
A2	$2.00\,p^{0.63}$	1-6	12.8
A3	$1.79\,p^{0.65}$	1-6	8.4

Qualitative and quantitative study of the phase structure of the MC condensed combustion products were performed on Shimadzu XRD diffractometer 6000 at CuKα- radiation, fig. 5.

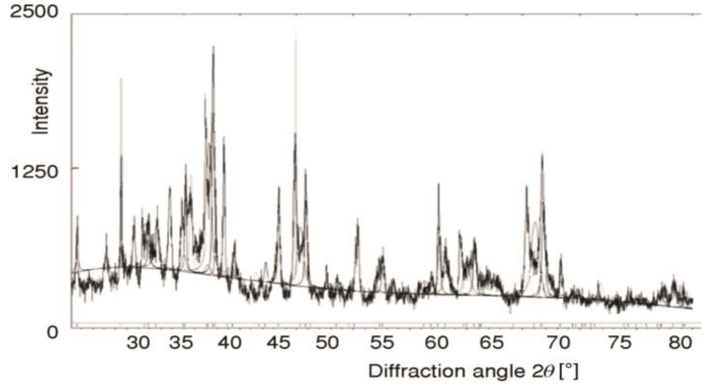

Figure 5. Qualitative X-ray diffraction pattern of condensed combustion products for MC containing aluminum powder type A2

Intensity of the lines is determined by the number of phases. Qualitative and quantitative (vol. %) phase analysis allowed to identify the following main phases in condensed combustion products in the MC, containing aluminum type A2:

$$Al_{2,78}O_{3,65}N_{0,35}\,(19.2\ \%),\ Al_{2,667}O_4\,(36.2\ \%),\ Al_2OC\,(15.8\ \%),\ \text{and C}\,(6.1\ \%)$$

The presence of carbon allows suggesting that increasing the oxidant excess ratio of MC original recipe one can regulate the output of condensed carbon in the combustion products.

Conclusion

The results of studies of the stationary burning rate in a pressure range of 0.04-6.0 MPa shows strong dependence of the burning rate *vs.* pressure. The exponent ν in burning rate law takes values of 0.63-0.73 depending on the type of aluminum powder in the MC.

Study of samples combustion at atmospheric pressure, out-of-doors, demonstrates the possibility to reduce the content of the condensed combustion products in MC containing aluminum A3 type up to 34% in comparison with compositions containing aluminum A2. The same trend is observed in the pressure range of 1-6 MPa.

The X-ray diffraction method gives chemical composition of condensed combustion products, their crystalline structure and volumetric content. Qualitative and quantitative phase analysis allows determining the presence of carbon in the condensed combustion products in MC, containing aluminum A2. This allows outlining possible methods to control condensed carbon content in the combustion products.

Nomenclature

p – pressure, [MPa]
u – burning rate, [mms^{-1}]
u_0p^ν – burning rate law
u_o – pre-exponent in the burning rate law
z – amount of condensed combustion products

Greek Symbols

α – excess oxidant ratio
ν – exponent in the burning rate law

Acronyms

A1 – nanosized aluminum powder Alex (uncoated aluminum powder)
A2 – alex, coated with a fluoropolymer Viton
A3 – alex, coated with heterocyclic organic compound 8-hydroxyquinoline
Alex – nanosized aluminum powder
AP – ammonium perchlorate
C_{al} – content of pure metal in aluminium nanopowder
DSC – differential scanning calorimetry
DTA – differential thermal analysis
MC – mixed compositions
nAl – aluminum nanopowder
SKDM-80 – inert fuel-binder
TGA – thermogravimetric analysis
XRD – X-ray diffractometer

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