

# Productions of Ultra-Fine Powders and Their Use in High Energetic Compositions

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## Abstract

Fine and ultra-fine powders are actively studied in pyrotechnics, explosives and propellants. The important questions are how to produce a powder with specified characteristics and how to use the powder produced.

This paper presents an approach to the powder production by the exploding wire method. The influence of initial conditions on the properties of powders is discussed. The basic factors are as follows: the level and the uniformity of the energy, dissipated in the exploding wire metal; the density and the chemical activity of the surrounding gas; the initial radius of wire. Electron Microscopes (Transmission and Scanning) and the Surface BET Method have been used for analyses. The production of ultra-fine powders based on such metals as Al, W, Zr, Cu, Fe, Ag, Co, In, Pt has been investigated.

Different surrounding passive gases (nitrogen, argon, xenon, and helium) were used for producing powders of pure metals. Samples were studied by chemical methods. X-ray Diffraction and Electron Diffraction methods were used for the determination of the phase compositions. Characterization included also Differential Scanning Calorimetry and Thermogravimetry in air with a heating rate of 100 K/min.

In summary, it was shown that the exploding wire method allows to produce ultra-fine powders of various metals. The results obtained can be applied directly to the production of powders with specified characteristics.

**Keywords:** Ultra-fine powders production, Propellant, Ignition, Burning rate

## 1 Introduction

The term “ultra-fine powder” (UF) means powder particles with an equivalent size of ten to a few hundred nanometers. Such a powder demonstrates deviations from conventional micrometer powders. First of all, it is connected with a high level of the surface area. The nanocrystalline microstructure is also important. If the ultra-fine powder is prepared under nonequilibrium conditions, the particles have a very high concentration of different defects (point defects, dislocations, grain boundaries, interphase boundaries, etc.). The size of nanostructure may be equal to

the same characteristic length (free path of electrons, coherent wavelength, magnetic domain size, and so on). Therefore, in any cases ultra-fine powders demonstrate unique features.

Nowadays, nanophase materials formed of ultra-fine particles or crystallites attract attention by the possibility to develop new technologies and to produce materials with new properties. This area opens a wide range of commercial applications. A currently interesting perspective route is the exploitation of ultra-fine powders as a component of energetic materials.

Recent investigations [1–3] show that the use of nanopowders allows to modify the burning rate, to increase the specific impulse and to prevent the agglomeration. Size, size distribution, morphology, and nanostructure of particles are very important characteristics, and they depend on the method of powder production.

To produce nanosized powders, the methods based on vaporization of metals followed by condensation and particle formation are being developed. Compared to other methods of vaporization, the electrical explosion of wires has the advantage of the direct conversion of electrical energy into heat. Besides, the pulsed heating provides high energy densities, high velocities of scattering and high rates of cooling of the substance. As a result, dimensional, structural, phase, defect, and other energy-saturated states are realized in the particles formed. The physico-chemical properties of nanophase materials and their behavior in chemical reactions and under physical actions essentially depend on the dimension and the defect structure of the particles or crystallites. Therefore, related comprehensive research provides a better insight into the phenomenon itself and promotes the creation of a technology for controllable production of powders and synthesis of new materials.

The purpose of the present paper is to highlight experimentally the possibilities of the exploding wire method for the production of ultra-fine powders, to comment its merits and demerits, and to describe some of the features of the powder produced. The results of the study are evaluated in the context of the problems of energetic materials and

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composite propellants. For research tasks and mass processing the technology must fulfil the following requirements:

- Production of powders in a wide range of metals and compositions
- A wide controllable size range of powders and controllable particle size distribution
- Prevention of spontaneous combustion and agglomeration
- Guarantee of the stability of the powder's physico-chemical features
- High level of productivity and economy
- Reproducibility of results

The increase of the propellant's energetic characteristics in the last 40 years is connected with the use of metal powders (generally aluminum) as one of the main components, which weight content in solid propellants (SP) reaches up to 22%. Experience of operation as well as extensive experimental and theoretical research on such propellants, carried out in Russia, USA, Western Europe and Japan, result also in large disadvantages due to the incompleteness of the metal combustion, "two-phase" losses of specific impulse and erosive effects on the nozzle walls.

The creation of a new generation of high-energy materials requires the search for new alternative approaches. The developments representing the most perspectives concern non metal containing solid propellants (SP) with new formulations of oxidizers and binders and the use of ultra-fine aluminum in composites. Recently identified problems of ignition and combustion of SPs and gels with ultra-fine aluminum are intensively investigated in a series of countries [1, 4–7].

In the present paper the results of an integrated experimental research on ignition and combustion of model composite propellants (solid and gels), containing a powder of ultra-fine aluminum with the mean size of particles less than 0.1 microns, are reported. The following experimental techniques and setups were used:

- The measurement of SP ignition time by the heated surface
- The measurement of SP ignition time by radiant heating
- The measurement of SP burning rate

## 2 Short Review

The success in the manufacturing technology of ultra-fine metal powders has allowed to pay attention to their capability of use as components of high-energy systems. The new manufacturing technology of ultra-fine metal powders by an electroexplosive method in atmosphere of various gases opens broad possibilities to use them as additives for controlling the rate of high-temperature oxidation of polymeric materials and compositions. The addition of ultra-fine aluminum powders increases the flammability of heterogeneous systems and their burning rate, reduces the agglomeration of particles and enables

regulations of an index  $\nu$  in the law of burning rate from pressure. Having a high specific surface (up to 12 m<sup>2</sup>/g) the ultra-fine metal powders can successfully compete with known catalysts and inhibitors of high-energy systems combustion [7, 9]. The high dispersivity of an aluminum powder (0.05–0.1  $\mu\text{m}$ ) practically does not influence the level of thermal flux in a condensed phase and the temperature of the combustion surface, however it increases a gradient of temperature at a surface from the direction of a gas phase [10–11]. Besides it is possible, that by adding 20% of aluminum a part of it can begin to react already in a reactionary layer of the condensed phase, as it was observed for other metals [12]. The research of Rogozhnikov and Andreev [13] has shown that the addition of fine aluminum ( $\approx 1 \mu\text{m}$ ) in ammonium perchlorate strongly increases flammability, ability of burning and propensity of transition to a convective combustion mode. The authors see the most probable reason of this influence in the interaction of aluminum with the primary decomposition products of ammonium perchlorate. The high thermal effect of the oxidation of aluminum generates high temperature gases which penetrate the powder and ignite it. The data on combustion and explosive characteristics of binary mixtures of an ultra-fine powder of aluminum (Alex) with  $\text{NH}_4\text{ClO}_4$ ,  $\text{KClO}_4$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$  are given in Ref. 9. The results on the ignition of structures containing Alex by a light flux are adduced in Ref. 7, where is shown that the addition of 18% Alex to the propellant allows to reduce twice the energy of steady ignition. The features of ignition and combustion of an ultra-fine powder of aluminum in oxidizing environments are investigated in Refs. 14 and 15. It was shown that the ignition of an aerosol (total oxygen concentration of 17–41%) occurs in a flow at temperatures of 473–573 K, which are much lower than those observed for the ignition of micrometer sized aluminum particles. The low temperature limit of ignition, first of all, is connected to the activity of an obtained aerosol of aluminum, with minimum width of an oxide layer on particles, which are not prohibitive for the evolution of a heterogeneous reaction and self-heating of particles, at an injection of oxygen in a flow. The combustion of Alex in atmosphere of air happens in two stages. The ignition occurs at the temperature of 623–823 K, then the particle achieves the temperature of the first stage, 1473 K, and after some delay the temperature is sharply increased up to 2273–2673 K. Previous papers show that irrespective of the way of obtaining an ultra-fine aluminum powder (method of vacuum metal evaporation or electroexplosive way) the particles are ignited at temperatures, which are characteristic for a combustion surface of high-energy materials.

It is known [16] that the condition of a catalyst particle surface plays an essential role in combustion processes. In Refs. 17–20 the catalytic efficiency of additives with a high specific particle surface on ignition and combustion processes of high-energy systems was investigated. It was shown that during combustion the accumulation of metal particles occurs on a combustion surface followed by agglomeration. The activity of metals as catalysts is determined by the size of

secondary particles. The agglomerates of initial particles of catalysts and their sizes depend only weakly on the specific surface of the primary particles [19]. It explains the low efficiency of the effect of catalyst with a high specific surface of particles on the burning rate of known heterogeneous systems [16, 21]. The suppression of the particle agglomeration process, for example, at reduced dispersivity of the oxidizer particles, increases the efficiency of combustion catalysts [22]. As the ultra-fine metal powders exhibit a lower tendency for agglomeration than ordinary (regular) ones their use as effective catalysts is possible.

### 3 Exploding Wire Technique

Different methods of ultra-fine powder preparation are developed, among them the exploding wire method is widely investigated by the researches of the USA, Germany, France, Japan, and Korea. The systematic investigations were initiated in Russia in the seventies [23–24].

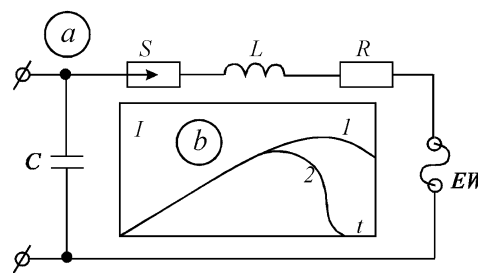
The greatest advantage of the exploding wire (EW) method over other evaporation techniques lies in the fact that the electric energy is transferred directly into heat. Depending on the process parameters, the products can be in liquid, vapor-droplet, vapor, or vapor-plasma state. The velocity of expansion of the wire material and its temperature may exceed 1000 m/s and 10000 K, respectively. For this reason, the method has been used to investigate the formation of particles at high heating and cooling rates [25–26]. Such conditions are nonequilibrium, and nanostructures of unstable energy can be formed.

Size, composition, and properties of powder particles depend on many factors. It is well known that the heating level, the uniformity of heat, and the pressure and type of the surrounding gas (inert or active) are the most important factors in the formation of particles, irrespective of the heating mode. Many processes resulting in polydispersity of the powder can disturb the heating uniformity in explosion.

#### 3.1 Experimental Setups

Experimental setups include the installations for powder production and facilities for the characterization of the powder produced. The electrical circuit used for the EW is shown in Figure 1, part a. To perform an explosion, the capacitor  $C$  is discharged through the wire to be exploded by EW. At the beginning of the process the capacitor is charged and the wire is automatically fed between the electrical contacts. Next, the switch,  $S$ , closes and the capacitor is discharged. The current flows along the electric circuit, producing Joule heating and explosive evaporation of the wire. After the first explosion, the process is repeated.

In Figure 1, part b, a typical oscillogram for the discharge current is shown. In this study the heating rate was controlled, and the conditions for fast electrical explosion [27] were fulfilled. To achieve fast electrical explosion the energy deposited into the wire must be of the order of the



**Figure 1.** The electric circuit of the set.

(a)  $L$  is the inductance and  $R$  the resistance of the circuit. (b) The current oscillograms for shorting (1) and during the electrical explosion (2)

sublimation energy and the heating time must be shorter than the time required for the development of instabilities (capillary and magnetohydrodynamic) but longer than the time required for the current propagation across the wire radius. Under the conditions of fast electrical explosion the heating occurs simultaneously and uniformly over the wire length and radius.

Explosions were performed in a hermetically sealed chamber filled with air, inert gas, nitrogen or a mixture of  $N_2 + O_2$ . The pressure was controlled and maintained at a designated level. The powders produced were collected by different ways and analyzed.

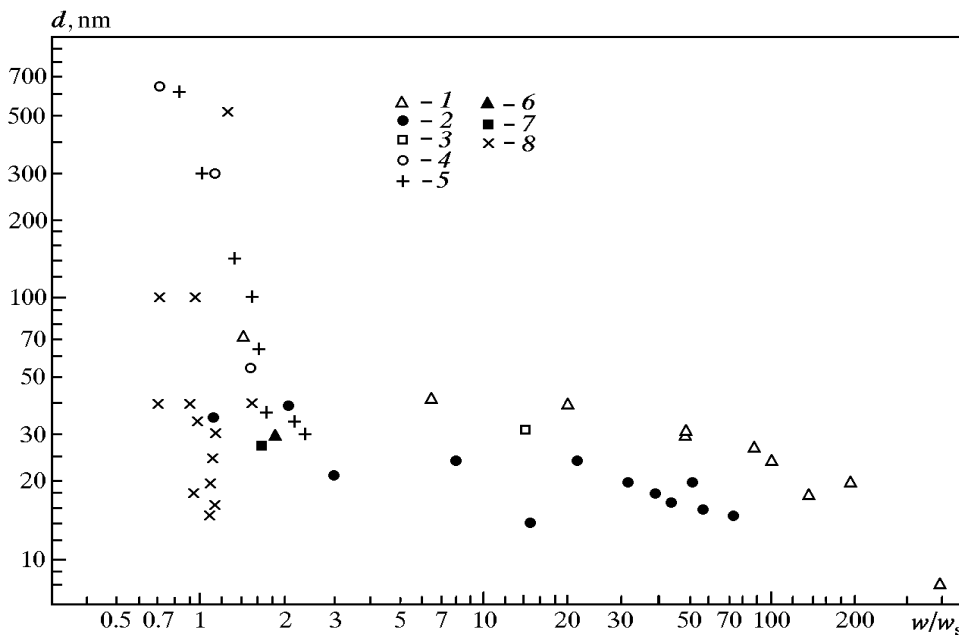
The major characteristic in powder production is the thermal energy introduced into the wire material. Depending on the energy density, the state of the explosion products can vary from liquid to plasma and the sizes and properties of the particles formed depend on the state of products.

#### 3.2 Particle Sizes and the Specific Energy Input

The energy density introduced in an exploding wire is one of the most important parameters. There exists a critical value,  $w_{cr}$ , such that with  $w < w_{cr}$  the explosion fails to occur. For the intermediate range,  $w_{cr} < w \leq w_s$ , the material state changes with increasing  $w$  from the droplet phase to the vapor-droplet phase and then to the vapor phase.  $w_s$  is the sublimation energy for a given metal. Figure 2 presents the particle diameter as a function of input energy density,  $d = f(w/w_s)$ , obtained from a variety of data from publications.

It is clear that the mean particle size  $d$  and the particle size distribution function vary with increasing input energy density. The function described above has two distinct regions (Figure 2). There is no accurate boundary between these regions. In the first region, the particle diameter varies by more than an order of magnitude while the energy content only doubles. This is related to the liquid-droplet-to-condensation transition in the mechanism for the particle formation [24]. Here  $d \sim (w/w_s)^{-3}$ .

In the second region  $d \sim (w/w_s)^{-1/3}$ , particles are formed only on the condensation nuclei. It should be additionally mentioned that in the input energy density range  $(w/w_s) \geq (1-2)$ , the condensation centers are ions. An increase of the



**Figure 2.** Particle diameter versus  $w/w_s$  (1, 2, 3 from Ref. 28). 1 – Is the count median diameter (CMD), Ag in air; 2 – Cu in air, crystal size; 3 – CMD for Cu in air; 4 – CMD for W in air; 5 – CMD for Cu in air; 6 – CMD for W in air; 8 – Surface median diameter for Al in air

input energy density results in an increase in the ions and in the expansion velocity. This leads to a decrease in the final size of the particles.

The data show that this technique allows to produce a powder with the size of 0.01 – 1  $\mu\text{m}$ . Figure 2 illustrates that to produce a powder with a particle size less than 0.1  $\mu\text{m}$  it is necessary to introduce in the wire material the relative value of energy  $(w/w_s) \geq (1 - 2)$ . The next important question is the power consumption for the production of ultra-fine powders.

### 3.3 The Energy Consumption

The specific energy released in a wire due to Joule heating is given by Eq. (1):

$$w = \int j^2 \rho dt / \gamma \approx \int \rho t / \gamma \quad (1)$$

where  $j$  is the current density in the wire,  $\rho$  is the specific resistance,  $\gamma$  is the density, and  $t$  is the time.

Considering the state of the exploded wire material, the process can be classified in two stages: the heating stage and the stage of explosion. The stages are different in the degree of change in density of the wire and of specific resistance. At the end of the heating stage, called “the initial point of explosion”, the explosive-like expansion and the abrupt increase in the specific resistance begin (the stage of the explosion). At the heating stage, the material’s resistance is mainly determined by the introduced energy, and here one can use the notion of “the integral of specific current action” [29 – 30] defined as

$$h = \int j^2 dt \approx j^2 t_h \quad (2)$$

Then, within the heating time  $t_h \approx h/j^2$ , the specific energy  $w = \rho h / \gamma$  is introduced.

The data above suggest that the current density is a significant factor in the explosion. The energy stored in the circuit,  $w_0 = CV_0^2 / 2Sl$ , and the “storage” of the specific action,  $h_0$ , are the essential factors. For example, it is impossible to explode a wire in a circuit where the stored energy and the stored action are not high enough:

$$h_0 = \frac{j_0^2 \sqrt{LC}}{2} = \frac{CV_0^2}{2zS^2} \quad (3)$$

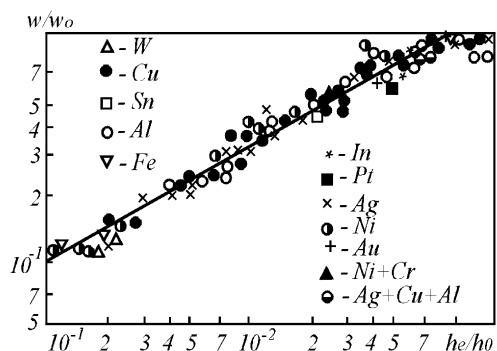
Here,  $z$  is the circuit impedance,  $j_0$  is the short-circuit current density,  $V_0$  is an initial voltage of the circuit,  $S$  is the wire cross-section, and  $l$  is the wire length.

As a result of processing of numerous experimental data, a simple relationship between the relative energy introduced into the wire during the first current pulse and the action ratio, common to all exploitable materials has been obtained [30]:

$$w/s = \sqrt{h_e/h_0}, h_e \leq h_0 \quad (4)$$

In Figure 3 the graph of the regression equation (4) and experimental points are plotted.

Figure 3 and Eq. (4) indicate that when the potential action of the circuit  $h_0$  is equal to the specific action integral  $h_e$ , i.e., when  $h_e/h_0 = 1$ , the matched explosion regime occurs [31]. In this regime practically all energy stored in the circuit



**Figure 3.** Dependence of  $w/w_0$  versus  $h_e/h_0$

**Table 1.** Properties of some metals.

Metal	Ag	Cu	Al	Ni	Fe	W
$w_s$ (kJ/g)	2.65	5.38	12.2	7.3	7.06	4.6
$h_e$	1.0	2.0	0.9	0.7	0.6	0.8
$K$	1.26	1.0	0.97	0.47	0.47	0.34

is released in the wire during the current pulse and the energy-transfer coefficient  $w/w_0$  is equal to one. From the above it should be clear that the EW technology is energy saving. Energy consumption is equal to the sublimation energy,  $w_s$ , of a given metal. Table 1 informs on the properties of some metals. On average, the energy consumption lies between 3–5 kWh/kg.

Using the dependence (4), one can determine not only the energy usability factor but also the overheating achievable under given conditions, i.e., the ratio of the energy introduced into the metal to the metal sublimation energy,  $w/w_s$ . A reverse problem (estimation of generator parameters needed to explode a given wire with required overheating  $w/w_s$ ) can also be solved. The integral of the specific action is easily estimated from the energy (temperature) dependencies of the metal specific resistance or by use of several current oscillograms, in accordance with Eq. (2). The values of  $h_e$  for some of the metals investigated with the current density  $\approx 10^7$  A/cm<sup>2</sup> are presented in Table 1.

Herein, the explosibility criterion of a metal,  $K$ , having practical importance in powder production, is also given. As evidenced by Eq. (4), the ratio  $\sqrt{h_e}/w_s = K$  is the integral characteristic of a metal determining its capacity to explode. Among the metals presented in Table 1, tungsten allows the lowest overheating because of its low  $h_e$  and its high sublimation energy. Compared to copper wires, the energy that can be introduced into a tungsten wire under the same conditions is 3 times lower. Nevertheless, it will be demonstrated below that the fast mode of electrical explosion permits to produce nanosized tungsten powder. Iron and nickel wires are exploded with equal overheating and the highest overheating can be produced on exploding a silver wire.

Investigations show that it is possible to decrease the size of particles and the energy consumption using conditions of

the fast electrical explosion and reduced pressure of surroundings.

#### 4 Powder Production at a Fast Electrical Explosion and Reduced Pressure of Surroundings

The sets based on the LC-circuit, Figure 1, part a, were used for this work. An exploded wire was delivered in automatic manner. A required gas-surrounding medium was maintained in the hermetically sealed explosion chamber. When a certain powder amount was produced, the process was stopped and the precipitated powder was collected and analyzed.

The specific surface area  $S$  of the samples was measured by the low-temperature adsorption method (BET). Particle shape and size distribution were determined by the transmission electron microscope. To define a phase and chemical composition of the samples, X-ray diffraction and analytic chemistry methods were used.

The production and features of powders based on Cu, Al, Ti, Pt, W, Fe, Zr and other metals have been investigated. Inert gases (Ar, He), their mixtures with oxygen, and nitrogen, ammonia, and mere air were used as surrounding media. In all cases the energy introduced into a wire material was measured by an oscillograph recording the current through the wire (Figure 1, part b).

##### 4.1 Fast Electrical Explosion

The velocity of Joule heating for a given metal, as follows from the Eq. (1), depends on the current density:  $\frac{dw}{dt} = j^2 \rho / \gamma$ . In Ref. 27 it was found that the energy density introduced into the wire material increases with increasing current density, and the current density defines the conditions of uniform heating. Therefore, the powder fineness was expected to depend on the energy and current density.

Some results are presented in Table 2. Data No. 1–3 of Table 2 for Cu wires demonstrate an effect of the introduced Joule energy on the powder fineness noted before. The variation of energy density within the range  $w/w_s = 0.50$ – $0.76$  by a factor of 1.5 varies the specific surface area of the copper powder from 3.2 to 8.9 m<sup>2</sup>/g. The similar behavior of the powder fineness with the introduced energy occurs at the explosion of platinum (Data No. 4 and No. 5 in Table 2) and other metals (Figure 2).

The results obtained for the explosion of indium wires (Data No. 11–16 of Table 2) demonstrate the effect of the current density  $j/j_{MHD}$  on the particle size of indium and aluminum powders. The current density  $j_{MHD}$  corresponds to the regime when sausage-type magnetohydrodynamic instabilities have time to develop. With similar introduced energies 0.8–0.85  $w_s$  the fineness of In and Al samples depends on the current density. On the other hand, the fineness of the sample I3 (Data No. 11) with the smaller introduced energy (0.62  $w_s$ ) is higher than that for the sample I2. In producing the sample I3 the current

**Table 2.** Experimental results.

No	Powder sample	Wire material	Powder material	Medium	$w/w_s$	$S$ [m <sup>2</sup> /g]	$j/j_{MHD}$
1	Cu 4	Cu	Cu	N <sub>2</sub>	0.5	3.2	
2	Cu 3	Cu	Cu	N <sub>2</sub>	0.65	6.0	
3	Cu 8	Cu	Cu	N <sub>2</sub>	0.76	8.9	
4	Pt 3	Pt	Pt	Ag + He	0.8	2.6	
5	Pt 5	Pt	Pt	Ar + He	1.1	9.6	
6	T 1	Ti	TiO <sub>2</sub>	O <sub>2</sub> (16%) + N <sub>2</sub>	1.5	43	
7	T 3	Ti	Ti	N <sub>2</sub>	1.0	30	
8	W 2	W	W	N <sub>2</sub>	0.8	2.4	
9	Zr 1	Zr	Zr	N <sub>2</sub>	0.8	5.7	
10	F 1	Fe	Fe <sub>3</sub> O <sub>4</sub>	air	1.1	20	
11	I 3	In	In	N <sub>2</sub>	0.62	3.6	1.33
12	I 1	In	In	N <sub>2</sub>	0.8	4.5	1.33
13	I 2	In	In	N <sub>2</sub>	0.8	3.0	0.47
14	I 6	In	In	N <sub>2</sub>	0.85	5.8	2.45
15	N89	Al	Al	N <sub>2</sub>	0.8	1.4	26
16	N90	Al	Al	N <sub>2</sub>	0.8	1.0	14

**Table 3.** Synthesis of powders in oxygen-containing gas.

Sample	$w/w_s$	$p$ [kPa]	O <sub>2</sub> [%]	$S$ [m <sup>2</sup> /g]	Al <sub>2</sub> O <sub>3</sub> ( $\gamma$ ) [%]
N5	1.0	20	0	29	0
N9	0.6	20	5	31	5 (100)
N59	0.6	47	5	34	15–20 (90)
A30	0.6	20	22	39	80–85
A13	0.6	33	25	49	100 (70)
A11	0.9	33	25	38	98 (70)
A12	0.25	33	25	45	95 (80)

density was higher than  $j_{MHD}$  and the heating was more uniform.

The obtained data suggest also that this method is more efficient due to the faster electrical explosion. Under these conditions the high deposited energies that are considerably higher than the sublimation energy are not necessary.

#### 4.2 Synthesis of Al-Al<sub>2</sub>O<sub>3</sub> and Al-AlN Compositions with Controlled Phase Ratio

The prevention of spontaneous combustion and agglomeration of particles is also an important question. Investigations performed have shown that the electrical explosion allows to synthesize the powders passivated by a thick surface layer of oxide or nitride. Thus, the activity of powders produced in the low-pressure nitrogen remains high.

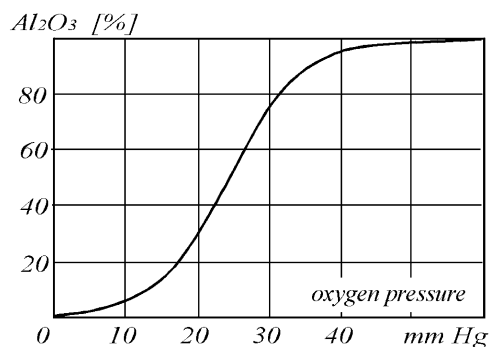
Table 3 gives the conditions for the electrical explosion of aluminum in a low-pressure oxygen containing gas and the properties of the produced powders. X-ray diffraction analysis indicates that there the  $\gamma$ -phase prevails and a quantity of the  $\alpha$ - and other phases are also present which was noted already in Ref. 32.

From Table 3 it can be seen that the oxygen content within the explosion chamber is an essential factor in the synthesis of oxides, and the phase constitution of the produced

powder can be varied from pure aluminum to various phases of oxides. Figure 4 demonstrates the experimental data of aluminum oxide yielded in dependence on the oxygen pressure within the chamber.

Table 4 shows the composition of powders produced in a low-pressure nitrogen containing gas.

Experiments [33, 34] indicated that molecular nitrogen is chemically inert at lower pressures. Nitrides in the powders of investigated metals are either absent or found as a trace amount. A quantity of fixed nitrogen was determined via decomposition of the samples in boiling sulfuric acid and in



**Figure 4.** Percentage of Al oxide output versus oxygen pressure (1 mmHg = 0.133322 kPa) in the chamber.

**Table 4.** Synthesis of powders in nitrogen-containing gas.

Sample	Gas	Pressure [kPa]	$S$ [m <sup>2</sup> /g]	Nitride content [%]
N1	N <sub>2</sub>	20	26	1.6
N2	N <sub>2</sub>	47	57	3.7
N27	N <sub>2</sub> + 10% NH <sub>3</sub>	47	59	57.9

**Table 5.** Thermogravimetry of the Al powders.

No	$w/w_s$	Gas	$S$ [m <sup>2</sup> /g]	$T$ [°C]	$\Delta m$ [%]
1	0.75	N <sub>2</sub>	22	520	5.5
2	0.75	Ar	18	516	9.8
3	0.75	Xe	9.3	525 ± 3	14.3 ± 1
4	1.0	N <sub>2</sub>	24	516 ± 3	19 ± 4
5	1.0	Ar + He	–	523	15.8
6	1.0	Xe	16.1	530	16

boiling concentrated alkali by the Kjeldahl method. Both the chemical and X-ray methods for analysis confirm this fact. The chemical analyses show that a detectable amount of AlN (more than 2% of mass) is synthesized at pressures exceeding 47 kPa. It is necessary to accentuate that Al is the metal readily producing nitride.

The dissociation energy of the nitrogen molecule N<sub>2</sub> (53.7 kJ/mol) is substantially higher than the sublimation energy of aluminum (18.8 kJ/mol), which is close to the energy density stored by the electrical circuit. The synthesis of the nitride requires an additional activation. Disturbances in stoichiometric contents of nitrogen in the reaction region at reduced pressures and a short time of the process are also of considerable importance.

A small addition of ammonia substantially increases the output of nitride (Sample 27 in Table 4). Nevertheless, the size of particles practically remains the same. These experiments indicate that a small quantity of nitride prevents the agglomeration of particles formed (cf. specific area  $S$  in Table 4). This fact may be useful in the study of coating particles in the combustion wave.

For comparing the activities of the powder samples in the combustion reaction, Differential Thermal Analysis (DTA) and Thermogravimetry were used. In this analysis, using 10 K/min, the onset temperatures of intense oxidation, the peak temperatures and the increase of mass,  $\Delta m$ , when oxidizing before the melting point, have been compared.

The samples produced in nitrogen with the low density of the introduced energy denoted as No. 1 in Table 5 begin intensely to oxidize at lower temperatures compared to the samples produced in inert gases with the same energy density. On the other hand, a passivation of the samples produced with higher introduced energy density in nitrogen is observed. The powders produced in low-pressure gas are highly active. This can be seen from a comparison of the peak temperatures  $T_{peak} = 520$  °C with published data: 553 °C and 573 °C [29], 580 °C [30], 605 °C [31].

### 4.3 Particle's Size and Morphology

The analysis of ultra-fine particles is a difficult problem. Measurements of the specific surface area of the powder provide only accurate information about the particle size if the morphology, smoothness and degree of equiaxialness of the particles are known. Transmission Electron Microscope (TEM) analysis is capable to give an information on these properties.

#### 4.3.1 The TEM Measurement Procedure

Investigations of the particle's size and morphology have been accomplished by 125 kV transmission electron microscopes. In preparation of the suspension industrial alcohol was applied on a slide and dried. Then a carbon layer was sputtered on the powder-slide using the vacuum deposition system. The resulted carbon replica was isolated by the use of water solution of gelatine, the gelatine was dissolved, and the carbon replica with the sputtered powder was placed on the copper mesh. The mesh with the powder was used as the sample for the electron-microscopic investigations.

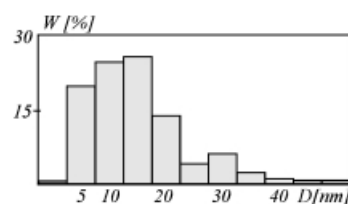
Medium sizes of the powder particles and their size distribution were analyzed with the help of microphotographs under  $250 - 300 \times 10^3$  magnification. The number of measured particles was in average 300–500 depending on the size uniformity of the powders. The numbers ( $N_i/N$ ) of particles within a given interval were plotted in histograms.

It should be taken into account that the particle size bigger than 5 micrometer limits this procedure, because such particles may be lost. Combining TEM and BET methods will be more informative.

#### 4.3.2 Titanium Powder

Particles of the titanium powder have an intricate spatial form with cross sections in a plane as a square, rectangle, triangle, and in some cases, hexagon shape. It can be supposed that a triangle prism (or hexagon which is extremely rare) may be such spatial one. The medium size of the particles is  $D = 14.24 \cdot 10^{-3}$  μm and the root-mean-square deviation  $\sigma = 8.11 \cdot 10^{-3}$  μm. The particle size distribution is monomodal and logarithmic-normal (Figure 5).

The specific surface area  $S$  of titanium powder is 30 m<sup>2</sup>/g (see Table 2, No 7). Under the assumption that particles are

**Figure 5.** Histogram of Ti particles size distribution.

**Table 6.** Structural-phase state of the Al powders and compositions of Al-Al<sub>2</sub>O<sub>3</sub>.

No	Sample	w/w <sub>s</sub>	P [kPa]	O <sub>2</sub> [kPa]	Al <sub>2</sub> O <sub>3</sub> [%]	D · 10 <sup>3</sup> [μm]	σ · 10 <sup>3</sup> [μm]	S [m <sup>2</sup> /g]
1	N5	1.0	20	0	0	37.0	21	29
2	N9	0.6	20	1	5	28.6	18.3	31
3	N59	0.6	47	2.3	15–20	28.5	12	34
4	A30	0.6	20	4.4	80–85	44.9	27.3	39
5	A13	0.6	33	8.3	100	37.0	19.2	49
6	A11	0.9	33	8.3	98	51.1	33.8	38
7	A12	0.25	33	8.3	95	41.6	26.7	45
8	N93	1.0	47	0	0	40.2	16.4	17.5
9	N94	1.0	47	0	0	48.3	30.5	11.0

spherical, the mean surface diameter of particles might be written as

$$d_s = \sqrt[6]{\gamma \cdot S} \quad (5)$$

For this case,  $d_s = 45 \cdot 10^{-3} \mu\text{m}$  is not far from the value obtained by TEM.

#### 4.3.3 Aluminum Powder

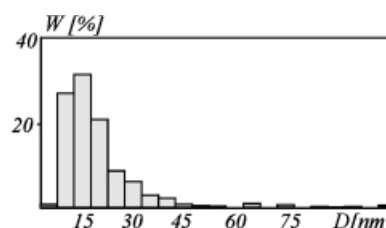
Observations indicate that the analyzed powder is morphologically a single-component and presented by spherical particles. Mean sizes of particles of the Al powder vary from 30 to 50 nm, that is, the particles are slightly coarser than particles of alumina powder.

As evident from the results presented in Table 6, the sizes of particles of the Al powder vary in a wider range than those of aluminum oxide powders. With that, a spread  $\sigma$  for the particles produced by an exploding wire with previously annealed coarse grains at a temperature of 730 °C is a maximum (Table 6 No 8, 9).

The electron microscopic diffraction analysis revealed that the powders produced in an oxygen-containing medium by the electrical explosion of Al wires are morphologically of two components and consist of a mixture of the particles in sphere and film forms. It is significant that the films are observed only in the aluminum oxide powders. In the Table 6 mean values of size  $D$  for the spherical particles without consideration of sizes for the crystallites that constitute the films are given.

Indication of the electron-diffraction patterns for the oxide powders has shown that there are two phases, namely,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The film crystallization (mean crystallite size is 6.5 nm) promotes the significant electron-diffraction pattern complication manifested in splintering of the first amorphous diffraction ring into assemblage of the point reflexes. With great crystallite sizes (16.5 nm) a presence of the film is unaffected on the electron-diffraction patterns structure. This fact suggests that the polycrystalline films have the same phase constitution as the spherical particles.

Films are obtained in both amorphous-crystal and nano-crystal state. Clearly, the given films (especially, the ones in

**Figure 6.** Histogram of tungsten particles size distribution.

amorphous-crystal state) are the structural unstable systems having physico-chemical properties, which vary with time and, as a result, a deterioration of the powder quality is possible.

#### 4.3.4 Tungsten

The particles of tungsten powder are of spherical form. The medium size of the particles,  $D$ , is of  $13.6 \cdot 10^{-3} \mu\text{m}$  and the root-mean-square deviation,  $q$ , is  $14.0 \cdot 10^{-3} \mu\text{m}$ . A wide particle size distribution and the presence of coarse particles is displayed clearly in the histogram of Figure 6. It results in a low value of the specific surface area:  $S = 2.4 \text{ m}^2/\text{g}$ ,  $dS = 0.13 \mu\text{m}$ .

## 5 Preparation Technique for Solid Propellants Compositions

AP/Al/HTPB (butyl rubber) compositions for model solid propellants (SP) were investigated. During SP manufacturing the contents and the dispersivity of oxidizer and metal were varied. Ammonium perchlorate was used as monofractional dispersivity, one less than 50 μm and one between 160–315 μm. The mixtures consisted of these fractions at various ratios. A mixer with self-cleaning blades was used. The batch time depends on how fast the stirring was performed and was usually 2–3 hours. Then, the vacuum pump was connected to the mixer and during 30–40 min a propellant was evacuated and cured at 343–345 K during 3 days. Catalysts of iron and soot were added in a quantity of 1%. The density of the cured samples was



**Table 7.** Compositions on the base of HTPB, ultrafine Al (UFA), ASD-1 (10–15  $\mu\text{m}$  Al).

Sample Nr.	HTPB [%]	AP [%] Dispersivity less than 50 $\mu\text{m}$	Al		
			Al [%]	Dispersivity [ $\mu\text{m}$ ]	Features of Alex manufacturing
29	18	62	20	0.01–0.1	Alex by explosion in Ar
31	18	62	20	10–15	ASD – 1
35	18	62	20	0.01–0.1	Alex by explosion in $\text{N}_2$
36	18	62	20	0.01–0.1	Alex by explosion in Ar / UF Fe explosion in Ar
37	18	62	20	0.01–0.1	Alex by explosion in Ar / UF Fe explosion in Ar
38	18	62	20	0.01–0.1	Alex explosion in Ar
39	18	62	20	0.01–0.1	Alex explosion in Ar, precipitated in kerosene
40	30	70	–	–	
41	30	70	–	–	UF Fe explosion in Ar
42	30	70	–	–	Regular Fe
43	18	62	20	10–15	ASD-1 / UF Fe + Soot (1:1)
44	18	62	20	0.01–0.1	Alex explosion in Ar / UF Fe + Soot (1:1)

**Table 8.** Ignition time delay of propellants, containing 1% of iron powder.

Sample Nr.	Ignition time delay [s]				
	563 K	578 K	593 K	608 K	623 K
36	32.8 $\pm$ 0.8	17.5 $\pm$ 0.6	11.2 $\pm$ 0.4	5.3 $\pm$ 0.2	2.0 $\pm$ 0.2
37	34.0 $\pm$ 1.2	18.2 $\pm$ 0.8	11.5 $\pm$ 0.6	5.5 $\pm$ 0.4	2.1 $\pm$ 0.2
41	27.6 $\pm$ 1.0	16.0 $\pm$ 0.8	7.5 $\pm$ 0.5	5.0 $\pm$ 0.3	2.0 $\pm$ 0.2
42	42.4 $\pm$ 1.2	28.4 $\pm$ 0.8	16.2 $\pm$ 0.6	8.0 $\pm$ 0.5	3.2 $\pm$ 0.2

**Table 9.** Ignition of propellants AP/HTPB.

Sample Nr.	Ignition time delay [s]				
	623 K	633 K	643 K	653 K	670 K
29	37.0 $\pm$ 2.0	25.2 $\pm$ 1.6	15.0 $\pm$ 0.6	9.4 $\pm$ 0.4	4.0 $\pm$ 0.4
31	37.0 $\pm$ 2.0	27.0 $\pm$ 2.0	14.6 $\pm$ 0.6	9.2 $\pm$ 0.5	4.4 $\pm$ 0.4
35	36.0 $\pm$ 3.0	23.5 $\pm$ 3.0	15.0 $\pm$ 1.0	8.4 $\pm$ 1.5	4.0 $\pm$ 0.5
38	34.0 $\pm$ 2.0	18.6 $\pm$ 2.0	11.0 $\pm$ 1.0	5.1 $\pm$ 0.6	2.6 $\pm$ 0.2
39	34.0 $\pm$ 2.0	20.4 $\pm$ 1.0	11.4 $\pm$ 0.5	6.2 $\pm$ 0.4	3.3 $\pm$ 0.2
40	65.0 $\pm$ 5.0	33.0 $\pm$ 2.0	16.0 $\pm$ 1.2	9.0 $\pm$ 0.8	–

1770  $\text{kg}/\text{m}^3$ ; the variance did not exceed 20  $\text{kg}/\text{m}^3$ . The composition of the propellants is shown in Table 7. For ammonium perchlorate a ratio of the fractions less 50  $\mu\text{m}$  and 160–315  $\mu\text{m}$  is 60:40. The catalysts were introduced into the systems based on HTPB.

## 6 Solid Propellant Ignition by a Heated Solid

The ignition of the model SPs was investigated by conductive heating by a metal unit in an environment of air at atmospheric pressure, in an interval of temperatures between 570 to 715 K. As heated surface a polished metal plate was used: stainless steel, diameter 50 mm and length 5 mm, molded in recess of a massive copper rod of a diameter of 70 mm and a length of 200 mm. The rod was heated up with the help of a nichrome spiral. In a plate distant 0.2–0.3 mm from the grinding end intended for a

contact to an investigated sample, a thermocouple was molded, which was calibrated in the range of 273–873 K with an error less than one degree. The SP sample consisted of a tablet (diameter 10 mm, height 5 mm) which was fastened to a rod. This freely moved in a vertical direction. The rod had an optimum weight ensuring the best reproducibility of the experiment ( $\approx 0.35$  kg). The moment of ignition was fixed on appearance of a flame; for the induction period the interval of time from the moment of the contact of the sample with the heated plate was considered.

The research results are shown in Tables 8 and 9.

The analysis of experimental results of SP ignition on the heated surface (Table 8 and 9) shows:

1. The addition of 1% of ultra-fine Fe essentially reduces the ignition delay time (for non-metal SP this effect is more expressed).

**Table 10.** Influence of the dispersivity and quantity of added metal on the value  $K$ .

Dispersivity of Al Value $K$ at the various weight contents Al [ $\mu\text{m}$ ]	Value $K$ at the various weight contents Al [ $\mu\text{m}$ ]			
	5%	10%	15%	20%
50–100	1.0	1.0	0.8	0.7
10–15	1.0	1.0	0.9	0.9
0.01–0.1	1.2	1.4	–	1.8

**Table 11.** Influence of the dispersivity of aluminum on the value  $K$  at various oxidizer excess ratios.

Dispersivity of Al [ $\mu\text{m}$ ]	Value $K$		
	$\alpha = 0.4$	$\alpha = 0.54$	$\alpha = 0.61$
50–100	0.7	1.0	1.0
10–15	0.9	1.0	1.0
1–2	1.2	1.2	1.5
0.01–0.1	1.8	2.0	2.2

- For SPs without Fe, the ignition delay time for SP containing ultrafine Al (UFA) is lower than for SP containing regular Al.
- With an increase of the surface temperature the ignition time delay decreases in all cases.

On samples with a heat-resistant binder (butyl rubber) and UFA, an explosive ignition was detected if a small-sized fraction AP (less 50  $\mu\text{m}$ ) was present. In a mode of explosive ignition the appearance of a flame is accompanied by a sharp sound effect and by fragmentation and combustion with high speed propagation of a heated layer through the sample part with sub-sequent extinguishing. Further, after heating the rest of the sample, the explosive character of ignition repeated. The detected mode of explosive ignition, evidently, is provoked by intensive oxidation and combustion of UFA in an upper-heated layer of the propellant.

It is known [14, 15] that with increasing dispersivity of an aluminum powder the onset temperature of its oxidation is reduced and at particle sizes of 0.08–0.2  $\mu\text{m}$  it is at the order of 570 K. Further, temperatures of a particle can amount to 1500 K and after some delay they can sharply increase up to 2300–2700 K. Ammonium perchlorate of a small-sized fraction together with the rather high temperature of the ignited surface promotes the evolution of an explosive propagation in a pre-heated layer. In propellants with reduced contents (up to 10%) of ammonium perchlorate of a small-sized fraction the explosive ignition is not observed. Lowering of the temperature interval of ignition similarly prevents the explosive ignition, which was achieved by replacement of the heat-resistant butyl rubber by the less heat-resistant and more active binder HTPB. However, addition of 1% UF Fe lowered the temperature of ignition by 50–90 K, but the mode of ignition (Sample Nr. 36, Table 8) did not change. It should be emphasized that a direct correlation between the mode of ignition and the burning rate of the given propellant at atmospheric pressure is not found.

The addition of an iron powder to the propellant results in lowering the ignition time delay (Table 8) and, the smaller the size of particles, the more effective is their influence (Samples Nr. 41, 42). UF Fe has lowered the temperature of ignition of a propellant with butyl rubber by 80–90 K, and of a propellant with HTPB by 40–50 K.

It is known [22] that the efficiency of catalysts decreases with the increase of the SP burning rate. Therefore, an evaluation of the efficiency of UF Fe on the ignition by an intensive heat supply, for example, at heating by a light flux in the range 50–300 W/cm<sup>2</sup> would be of interest. Such a high rate of heating can be realized by a radiation heating “Uranium” [8].

## 7 Burning Rate of Solid Propellant

### 7.1 Technique of SP Burning Rate Determination

The SP burning rate at increased pressure, 1–8 MPa, was determined in a bomb of constant pressure in argon atmosphere on samples with 10 mm diameter and 30–40 mm length isolated outside by a PVC tape. The burning rate at atmospheric pressure was determined in air. Either cured samples were used, or molded ones from of uncured mixtures and made in the sleeve from two layers of a tracing paper. The burning rate was measured by recording the burning of wires; error of measurement is 10 %.

The influence of aluminum was characterized by the efficiency ratio  $K$ , i.e. the relation of the metallized SP burning rate to the non-metallized SP burning rate. Similarly, the efficiency of the replacement of aluminum with a dispersivity of 10–15  $\mu\text{m}$  (brand ASD-1) by Alex 0.01–0.1  $\mu\text{m}$  was obtained. For cured samples the exponent  $\nu$  in the burning rate law was determined.

### 7.2 Combustion of SP at Atmospheric Pressure

For finding out the mechanisms of the influence of aluminum with a particle size of 0.01–0.1  $\mu\text{m}$  tests were conducted at atmospheric pressure. In Table 10 the relations of influence ( $K$ -value) of the dispersivity of aluminum and the quantity of added metal are listed with an excess of the oxidizer of 0.4.

The listed data show that the addition of large particles of metal results in a lowering of the burning rate. The effect is the stronger, the higher the content of aluminum is. Alex increases the burning rate, and the efficiency grows in accordance with the increase of the contents in the SP.

In Table 11 the efficiency of aluminum on the value  $K$  for systems with various excesses of oxidizer  $\alpha$  is shown. 20 % of metals were added to the SPs.

In Table 12 the data on combustion of SPs are listed at  $\alpha = 0.54$ , the SPs containing 20% of aluminum varying the dispersivity of ammonium perchlorate (AP). Here the values of the efficiency of Alex in relation to Al with a dispersivity of 10–15  $\mu\text{m}$  are shown.

**Table 12.** Influence of the dispersivity of the oxidizer and the dispersivity of aluminum on the SP burning rate at atmospheric pressure.

Dispersivity of Al [ $\mu\text{m}$ ]	Burning rate [mm/s]			
	AP < 1 $\mu\text{m}$	AP < 50 $\mu\text{m}$	AP 160–315 $\mu\text{m}$	AP 300–400 $\mu\text{m}$
10–15	2.0	1.8	1.6	1.3
0.01–0.1	No burning	No burning	2.0	2.2
Ratio K	–	–	1.25	1.69

**Table 13.** Influence on the burning rate and the value *K* of various production environments of Alex

Atmosphere for Alex manufacturing	Burning rate [mm/s]	<i>K</i> 10–15 $\mu\text{m}$	<i>K</i> (Alex)
Argon	1.3	1.4	1.0
Argon	1.4	1.5	1.0
Nitrogen-argon (1:3)	1.3	1.4	1.0
Nitrogen-argon (1:1)	1.7	1.9	1.36
Argon, storage in air 6 months	1.6	1.8	1.28

**Table 14.** Influence of catalysts on the burning rate of SP based on HTPB

SP	Burning rate [mm/s]				
	Initial	Soot	Regular Fe	UF Fe	Soot + UF Fe (1:1)
Without Al	1.23	1.60	1.84	2.74	2.90
20% Al, 10–15 $\mu\text{m}$	1.67	–	–	–	2.90
20% UFA	3.54	–	–	5.40	3.50

**Table 15.** Efficiency of catalysts effects on various SPs.

SP	Value <i>K</i>			
	Soot	Regular Fe	UF Fe	Soot + UF Fe (1:1)
without Al	1.30	1.49	2.22	2.36
20% Al, 10–15 $\mu\text{m}$	–	–	–	1.74
20% UFA	3.54	–	1.52	1.52

From the data of Table 12 it is obvious, that the SPs containing small-sized oxidizer and metal do not support the combustion at atmospheric pressure. The increase of the size of ammonium perchlorate particles in systems containing aluminum particles with a size of 0.01–0.1  $\mu\text{m}$  results in a noticeable increase of the burning rate. When the size of Al particles is 10–15  $\mu\text{m}$  the burning rate of compositions decreases in accordance with the increase of the content of the oxidizer, at the addition of a fine oxidizer it grows. In Table 13 the data related to the influence of the manufacturing and storage conditions of Alex on the burning rate of SPs with a factor of excess of an oxidizer 0.40, containing 10% of metal, are listed

Therefore, the contact of aluminum particles with a certain volume of nitrogen at the moment of manufacturing or at long duration of storage in air increases noticeably the efficiency of UFA during the combustion of SP based on AP. In Table 14 the experimental data on the influence of soot and iron catalysts on the burning rate of SP based on HTPB are illustrated. The components added did not exceed 1%. As components were used soot of a brand MP-75 and metal iron of two kinds, large regular particles and ultra dispersed

iron with the particle sizes of 0.01–0.1  $\mu\text{m}$ . The oxidizer excess is 0.4. In Table 15 the efficiency of the addition of catalysts in various SPs is shown.

From these data it follows that it is most effective to add the components to non-metal SPs. The presence of metals reduces the influence of the catalysts the stronger the smaller the particle sizes of the latter are. So, the addition of soot, increasing the burning rate of non-metal SP in 1.3 times, does not influence the compositions containing 20% UFA. The efficiency of the addition of UF Fe decreases from 2.2 for non-metal SP to 1.52 for SPs containing UFA.

### 7.3 Combustion of Solid Propellants at Increased Pressure

In Table 16 the data on the efficiency of the addition of 10% aluminum in a SP of various dispersivities in comparison with non-metal SP are shown.

From the listed data follows that the efficiency increases with decreasing sizes of the metal particles and practically does not depend on the excess of the oxidizer.

**Table 16.** Influence of the oxidizer content and the size of aluminum particles on the SP burning rate.

$\alpha$	Al dispersivity	Value $K$			
		1 MPa	2 MPa	4 MPa	6 MPa
0.40	ASD – 10–15 $\mu\text{m}$	1.2	1.6	1.6	1.9
0.40	Alex 0.01–0.1 $\mu\text{m}$	2.4	2.6	2.8	2.9
0.54	ASD – 10–15 $\mu\text{m}$	1.2	1.5	1.7	2.0
0.54	Alex 0.01–0.1 $\mu\text{m}$	2.3	2.6	2.7	2.8

**Table 17.** Influence of metal content and particle size on the burning rate and  $\nu$  value.

Al [%]	Al dispersivity [ $\mu\text{m}$ ]	Burning rate [mm/s]				Value of $\nu$	Pressure [MPa]
		1 MPa	2 MPa	4 MPa	6 MPa		
0	–	1.8	2.1	2.9	3.2	0.39	1–6
5	10–15	2.8	3.6	3.9	–	0.26	1–4
5	0.01–0.1	3.4	4.4	5.2	–	0.35	1–4
10	10–15	2.8	3.4	4.6	5.0	0.39	1–6
10	0.01–0.1	3.9	5.4	8.5	9.5	0.58	1–6
20	10–15	3.0	3.5	4.2	4.9	0.34	1–6
20	0.01–0.1	6.1	8.0	10.3	12.8	0.50	1–6

**Table 18.** Values of  $K$  and  $\nu$  at  $\alpha = 0.40$ .

Alex [%]	Value $K$				Increasing $\nu$
	1 MPa	2 MPa	4 MPa	6 MPa	
5	1.2	1.2	1.3	–	1.35
10	1.4	1.6	1.8	1.9	1.49
20	2.0	2.3	2.4	2.6	1.47

**Table 19.** Influence of metal dispersivity versus burning rate and  $\nu$  value.

Al dispersivity	Burning rate [mm/s]					$\nu$	
	1 MPa	2 MPa	4 MPa	6 MPa	8 MPa	1–6 MPa	1–8 MPa
–	2.2	3.3	3.5	3.9	4.1	0.39	0.39
10–15 $\mu\text{m}$	3.8	4.9	6.0	6.7	8.4	0.39	0.43
0.01–0.1 $\mu\text{m}$	4.8	7.2	10.7	12.8	16.9	0.64	0.64

**Table 20.** Values of  $K$  and  $\nu$  for SP at  $\alpha = 0.54$ .

Alex [%]	Value $K$					Increasing $\nu$	
	1 MPa	2 MPa	4 MPa	6 MPa	8 MPa	1–6 MPa	1–8 MPa
10.0	1.3	1.5	1.8	1.9	2.0	1.64	1.49

In Table 17 the influence of the metal content and its dispersivity of the Al particles on the burning rate and its dependence on pressure for SPs with an excess of oxidizer 0.40 are shown. In Table 18 the sizes of factors  $K$  and  $\nu$  for formulations containing various quantities of Alex are listed.

The obtained data show that the addition of Alex results in an increase of the burning rate in the investigated pressure interval. The efficiency of Alex addition grows in accordance with the increase of the contents of metal in SP up to 1.4–1.5 times. The addition of aluminum particles with a

size of 10–15  $\mu\text{m}$  practically does not influence the exponent in the burning rate law. In Table 19 the data on the influence of 10% of aluminum of various dispersivities on the SP combustion with an excess of oxidizer 0.54 are listed. Simultaneously, the characteristics of combustion of non-metal SP at  $\alpha = 0.54$  are compared and in Table 20 the values of factors  $K$  and  $\nu$  for SP containing Alex at  $\alpha = 0.54$  are shown for various pressures.

Therefore, in SPs with high contents of oxidizer the addition of small Al particles results in an increase of the burning rate which occurs the stronger, the smaller the size

of the added metal particles is. The exponent in the burning rate law practically does not vary at the addition of aluminum with dispersivity of 10–15  $\mu\text{m}$ . At the addition of metal with particle sizes of 0.01–0.1  $\mu\text{m}$  it is increased by 1.5–1.6 times.

## 8 Discussion

Research on uncured SP samples, containing aluminum of various dispersivities in quantities of 5% up to 20% (Table 10) confirmed earlier obtained results for SP containing UFA. At addition of more than 10% of big aluminum particles a noticeable lowering of the burning rate is observed (up to 30%). A possible reason can be the incomplete combustion of metal and a related reduced heat flux from the combustion zone.

UFA, in agreement to Ref. 8, is ignited at a distance  $\approx 5$  mm near to the surface of combustion, i.e. is ignited and burns completely at once as soon as it is exposed on a combustion surface. This effect, evidently, explains the increase of the SP burning rate by the addition of UFA. Besides the catalytic influence of UF particles onto the high-temperature oxidation (combustion) of polymeric fuels, this influence is the stronger, the smaller the metal particle size is. This effect does not depend on an excess of an oxidizer of a considered system (see Table 11). The steady combustion at normal conditions is characteristic only for SP formulations containing rather big oxidizer particle sizes, not less than 160–315  $\mu\text{m}$  (Table 12). Probably in this case the formation of a pre-heated layer in a sample is the main reason. In case of a small-sized oxidizer the warm up layer is broader, but the temperature is insufficient for the decomposition of the heat-resistant butyl rubber, and does not allow to realize the process of steady combustion. However, experimental data are not sufficient to draw correct conclusions and further research in this direction is necessary.

In accordance with data from Ref. 9, the properties of UF metals properly depend on conditions of manufacturing and storage. Therefore, the influence of these conditions on the SP burning rate (see Table 13) was studied. The obtained experimental data show that the presence of nitrogen in the manufacturing environment or in the long duration storage of a powder in air results in a sharper increase of the burning rate, in comparison to that in argon atmosphere.

The reason can be the derivation of aluminum nitride in the combustion products, that result simultaneously in sharp increase of the temperature and the burning rate of the metal [35].

Concerning the influence of catalysts on the investigated systems (Tables 14 and 15), the greatest effect is observed by addition of catalysts to non-metal SP formulations. In SPs containing UFA the efficiency of catalysts of iron and soot decreases. Probably, the formulations containing UFA burn with the higher rate and at higher temperatures. However, for the description of catalysis, even at a qualitative level, additional experiments, i.e. extension of a circle of catalysts, are necessary.

The analysis of experimental data (Tables 16–20) shows that the efficiency of the size of aluminum particles does practically not depend on an excess of an oxidizer and is increased in accordance with decreasing sizes of metal particles. So, by variations of the sizes of aluminum particles with dispersivities from 10–15  $\mu\text{m}$  to 0.01–0.1  $\mu\text{m}$  the burning rate is increased by 1.4–2.0 times. The highest increase is observed at reduced pressure of the order 1 MPa. The efficiency of UFA is increased in accordance with the increase of the contents in the SP formulation. Simultaneous use of UFA results in an increase of the exponent in the burning rate law. Aluminum with a dispersivity of 10–15  $\mu\text{m}$  practically does not influence the burning rate law. The obtained findings do not contradict the data reported in Ref. 9.

## 9 Conclusions

A study beginning from the conditions requested for ultra-fine powder production by exploding wires, and investigation of their physico-chemical properties and reactivity allowed to formulate the engineering conditions for the production of powders with given requirements. The following conclusions were achieved.

The particle formation is a complex process depending on several parameters such as the value of energy introduced into the wire, current density, ambient gas pressure and heat effect of chemical reactions. These factors must be considered to interact in a complex manner.

It has been demonstrated that it is possible to produce powders of pure metals using nitrogen at low pressures. Nitrogen is a promising gas since it has a higher electric strength and a lower mass density than those of inert gases, and this allows to increase the powder fineness. Metal powders produced in nitrogen exhibit a rather high activity at oxidation. On the other hand, nitrogen prevents particles from agglomeration.

The general character of relationships between the size of oxide particles and the gas pressure, the oxygen content of the gas, and the introduced energy density has been revealed. A detailed parametric study is necessary to optimize these variables. To obtain complete and accurate information about morphology and size it is necessary to use a variety of methods to analyze ultra-fine powders.

The main demerit of the method is its poly-dispersity, i.e. its too broad size distribution and the presence of coarse particles. It can be seen from the difference of  $D$  and  $d_s$ . Nevertheless, firstly it has been shown that technology allows to produce nano-sized tungsten powders, although tungsten is a metal difficult to explode.

The EW method is environmentally safe and does not require excess energy expenditures. The electrical explosion of a wire at reduced pressure opens new possibilities in the production of ultra-fine powders. Further investigation needs to be undertaken to determine the stability of powder features and to study the behavior of powders coated by oxide and nitride as a component of energetic materials.

The influence of UFA, UF Fe and soot on the high-temperature oxidation of butyl rubber and HTPB in combustion and ignition regimes was considered. It was shown that the addition of UFA results in an increase of the burning rate both at atmospheric pressure and in an interval of 1–8 MPa. The effect practically does not depend on a factor of excess of an oxidizer of the composition and is increased in accordance with the growth of the contents of UFA in SP.

The consideration of the influence of catalysts of iron and soot on the investigated processes has shown that the UF catalysts are most effective for non-metal systems. The efficiency of catalysts is reduced at addition of UFA into the system.

For some formulations of SP a mode of explosive ignition is characteristic. The mechanism of this phenomenon is not clear and requires further research.

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