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Investigation of Al Nanopowders Produced by the Exploding Wire Method*)

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Abstract: The impetus for this research came from fundamental and applied questions connected with specified characteristics of Al nanopowders, theirs controlled syntheses and passivation, and their activity as high energetic ingredients in solid propulsion and in aluminum-water gels. Different conditions of powder syntheses by the exploding wire method and powder passivation were used: syntheses at low-pressure gases (Ar, N_2, CO_2) and passivation in atmospheric-pressure gases (air, N_2, CO_2). Investigations of particle sizes and morphology have been accomplished with a 125-kV transmission electron microscope. The specific surface area S has been determined by BET method. Particles are predominately spherical, BET surface area was of 15-40 m^2/g. The composition and surface properties of nanopowders produced under various conditions were studied by mass-spectroscopy techniques at temperatures of 0-450 °C, by electron and X-ray diffraction methods, and by elemental analysis methods. To determine activities of the powder samples in the combustion reactions, the Differential Thermal Analysis, Thermogravimetry, and reaction with water were conducted. Active metal contents have been determined from amount of impurities and hydrogen extracted in direct thermohydrolysis of nanopowders by distilled water at 60 °C. Kinetics of gas evolution was determined therewith and shows two steps. Active aluminum content is within range of 16-80%. A composition of adsorbed gases and dynamics of desorption in vacuum have been investigated too. Correlation between conditions of nanopowder syntheses and specific surface and chemical activity in reaction with water and maximum oxidation degree have been determined.

Keywords: nanopowders, characterization, passivation, oxidation, combustion

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Introduction

Different methods are developed and used for nanosized metal powder production: laser, electron-beam, Gen-Miller, electrical explosion, plasma-chemical, and others. Among them the exploding wire method has the advantage of direct conversion of electrical energy into heat with high efficiency [1]. Besides, the pulsed heating provides high and uniform energy densities, high velocities of expansion and high rates of the substance cooling. As a result, dimensional, structural, phase, defect, and other energy-saturated states are realized in the particles formed.

Growing interest in nanopowders is stimulated by the possibility to increase the inflammability, the burning rate, and the completeness of metal combustion and to decrease the agglomeration. The area of investigations includes metallized solid [2], liquid [3], and metallized gelled propellants [4].

The purpose of the present paper came from fundamental and applied questions connected with specified characteristics of nanopowders produced by the exploding wire method, and their activity as high energetic ingredients in solid propulsion [2] and aluminum-water gels [5-8].

The structure of the paper is as follows. Section 2 describes the methods and techniques of investigation, different apparatus and physico-chemical methods used for analysis of powders. Section 3 dwells on a size of particles and crystallites. Section 4 is devoted to constitution of powder samples. Section 5 describes the results of investigation of powder activity in reactions with air and hot water. Powder fineness effect is described as well. Section 6 demonstrates powder fineness effect on combustion of Al/gelled water mixtures. It has been established that the combustion rate sufficiently grows when a high-dispersed powder is used.

Experimental Methods

Experimental setups include the installation for powder production and facilities for characterization of the powder produced.

Engineering conditions

Engineering conditions for production of powders by the exploding wire method with given requirements are formulated in the papers [1, 9]. The investigations performed have shown that the electrical explosion allows synthesizing the powders passivated by oxide or nitride [9-11] as well as

by oxycarbide and by the layers of absorbed gases [8]. With that, the activity of powders remains high.

The major characteristic in powder production is the thermal energy introduced into the wire material. In this study, the energy density was close to the sublimation energy of aluminum, and the conditions of uniform Joule heating of a wire [9, 12] were used.

Determination of dispersivity of powders

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

The specific surface area S_{BET} of the samples was measured by the low-temperature adsorption method (BET).

The particle shape and size distributions were determined using the 125 kV TEM. In preparation, the suspension powder – 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 gelatin, gelatin 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 subject for TEM investigations. The mean diameters D and the standard deviation σ were calculated from TEM data. Medium sizes of the powder particles and their size distribution were analyzed with the microphotographs with (250-300) 10^3 magnification. The results are given below. The number of measuring particles is averaged 300-500 depending on the powder size uniformity. The algebraic number (N_i/N) of particles with the size of the given interval was plotted in histograms.

It is necessary to have in view that this procedure is limited by the particle size of more than 5 micrometer, because such particles may be lost. So, the results will be distorted. In this connection, common measurements by TEM and BET methods will be more informative.

The X-ray diffraction (XRD) method was used to determine mean sizes of regions of coherent scattering (D_{RCS}) for major phases. The coherent scattering regions (RCS) for produced powders were determined on the data of roentgen lines broadening at small angles.

Determination of powder composition

The composition and surface properties of nanopowders produced under

various conditions were studied by mass-spectroscopy techniques at the temperatures of 0-450 °C, electron and X-ray diffraction methods (XRD).

The phase analysis and determination of the fine crystal structure parameters of powders have been implemented by means of XRD apparatus DRON-UM1 with filtered copper radiation K_{α}. A relative error in determination of the phase constitution in the powder was under 10% and in determination of the parameters it was under 0.1%.

Active aluminum mass content, Al %, was determined by measuring the hydrogen volume, which was formed in reaction of aluminum with solution of sodium hydrate.

The composition of adsorbed gases has been determined by heating of samples in the vacuum of 10^{-7} at various temperatures as well as during linear heating with ramp function of temperature.

Investigation of powder activity in oxidation reactions

To determine activities of the powder samples in the combustion reactions, the Differential Thermal Analysis (DTA), Thermogravimetry (TG), and reaction with hot water were conducted.

DTA and TG were implemented in air with the heating rate of 5 °C/min.

The special gasometric device was used for determination of gas volume extracted during the reaction of aluminium powder with hot water. Mixtures 2.7 mg of Al and 10 g of distilled water were placed in the cell thermostated under 60 °C, and the volume of gas released has been calculated using the bubble recorder.

In reactions with hot water, aluminium oxidized and is transformed to the oxyhydroxide. Final product has been analysed using BET and TG methods. TG was implemented in air at the temperature range of 20-1000 °C and heating rate of 10 °C /min.

Investigation of combustion of nanoaluminum-gelled water compositions

Experiments were conducted in a close manometric bomb of 5 liter filled with argon at a constant controlled pressure. Mixtures were placed in quartz glasses of 10 mm diameter and 35 mm length and were ignited by a nichrome spiral. At least 3 tests or more were performed for one experimental point with the given conditions.

The combustion rate was under determined by two photodiodes with the distance between them of 20 mm. Both photodiodes were coarsened and adapted through two observation slits to radiation from a combustion wave. A millisecond stopwatch was started by the first photodiode and stopped by the second one.

The size of particles and crystallites

The following types of powder markings are assumed: the gas used as medium for a wire explosion is noted first, and the gas used for the powder passivation is noted through the slant line. For instance, N_2/CO_2 designation corresponds to the powder produced in nitrogen and passivated by carbon dioxide etc. The specific surface of powders varies from 16 to 38 m^2/g. The particles are predominantly spherical (Figures 1, 2).

If the particles are spherical, one can determine the mean-surface diameter d_S as $d_S = 6/\gamma S_{BET}$ where γ is the density, for Al $\gamma = 2.7$ g/cm^3. These data for some samples are placed in Table 1 together with the mean diameters D, the standard deviations σ, determined from TEM photos, and mean sizes of regions of coherent scattering (D_{RCS}) evaluated from XRD lines.

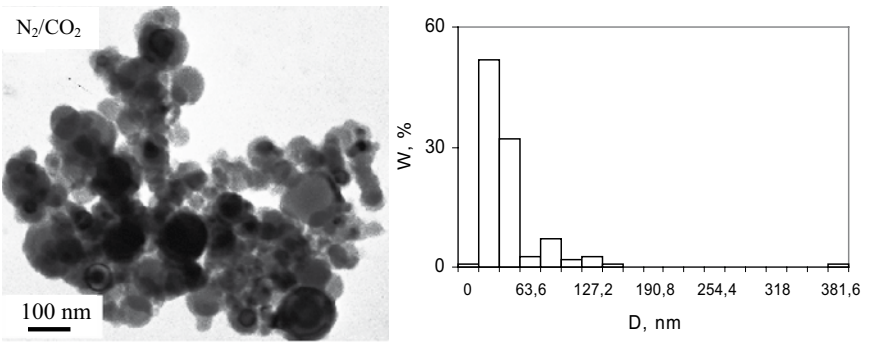

Figure 1. TEM photo and size distribution of powder sample N_2/CO_2.

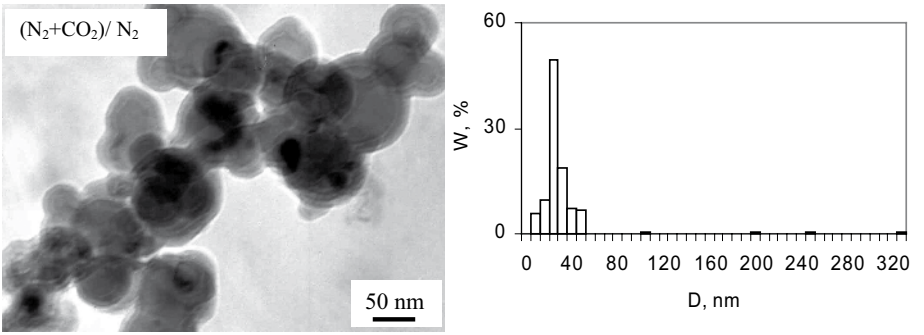

Figure 2. TEM photo and size distribution of powder sample $(N_2+ CO_2)/CO_2$.

Table 1. Size of particles and crystallites

Sample	S_{BET}, m^2/g	d_S, nm	D, nm	σ, nm	D_{RCS}, nm
N_2/air	17.5	127	40.3	16.4	29
N_2/CO_2	21.0	106	40.4	6.1	30
N_2+CO_2/N_2	34.3	65	32.4	4.7	32.5

Detailed comparison between values D, σ, and D_{RCS}, shows that the particles of N_2+CO_2/N_2 sample are monocrystal, and comparison between values d_S and D shows that the particles of this sample are slightly agglomerated. Ideal case, $d_S = D$, may be observed with oxide or nitride particles because particles of pure metals are easy agglomerated during preparation and storage.

Constitution of powder samples

Different conditions of powder synthesis by the exploding wire method and powder passivation were used: synthesis in low-pressure gases (Ar, N_2, CO_2), passivation in atmospheric-pressure gases (air, N_2, CO_2).

A constitution of gas shells and desorption dynamics were investigated by using the mass spectrometry method and by measuring the pressure of releasing gases in the interval of 0-450 °C on heating in vacuum at constant temperatures and under the fast (to 50 K/min) linear dynamic heating.

The composition and some properties of powder samples produced and passivated in various gas mediums are summarized in Table 2.

Table 2. Results of Al nanopowders analysis

Sample	S, m^2/g	Al, %	Water, mass %	Sum of gases, mass %	XRD, volume %			
					Al	Al_2O_3	AlN	$Al\ N_5O_{14}$
N_2/N_2	18.2	75.4	6.4	1.7	96		4	
N_2/CO_2	21.0	70.7	0.4	2.9	90	5		~5
$(N_2+CO_2)/N_2$	34.3	60.7	1.5	5.2	91	9		

The percentage content of pure aluminum (Al %) was determined by a volumetric method in which the volume of hydrogen, as a result of reaction of Al with solution of sodium hydrate, has been measured. The percentage volume contents of Al, Al_2O_3, AlN, and $Al\ N_5O_{14}$ were determined by XRD method.

It was found that the composition of desorbed gas components is highly

changed with the temperature increase and depends on the surroundings of preparation and passivation.

Tables 3 and 4 give the composition of gases desorbed in vacuum under different temperatures.

Kinetics of gas evolution shows two steps (Figure 3).

Table 3. Sample N_2/CO_2: Composition of desorbed gases at different temperatures (T °C), volume %

T, °C / Gas	0	50	100	150	200	250	300	350	400
N_2	73.5	79.6	88.4	91.1	82.0	64.7	86.7	96.0	82.8
O_2	8.2	8.0	5.5	4.7	8.8	5.6	4.9	1.9	15.5
Ar	0.0	0.0	0.02	0.01	0.0	0.0	0.0	0.0	0.0
CO_2	2.3	1.6	0.4	0.3	0.2	0.1	0.0	0.0	0.0
H_2O	16.1	11.8	5.7	3.9	6.8	23.0	6.3	2.1	1.7
NH_3	0.0	0.0	0.0	0.0	1.2	9.7	2.1	0.0	0.0

Table 4. Sample CO_2/CO_2: Composition of desorbed gases at different temperatures (T °C), volume %

T, °C / Gas	0	50	100	150	200	250	300	350	400
N_2	35.3	15.6	26.0	15.8	13.3	9.5	6.7	4.9	4.1
O_2	11.8	4.7	6.4	6.0	3.6	2.6	1.8	1.3	0.8
Ar	0.0	0.0	0.1	0.2	0.05	0.0	0.0	0.0	0.0
CO_2	48.8	73.3	57.1	72.8	67.0	53.8	73.1	92.1	92.3
H_2O	4.1	7.4	6.4	5.2	16.0	34.1	18.3	1.7	2.8

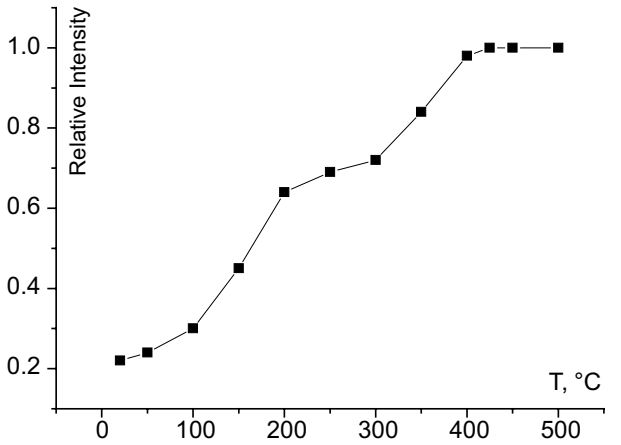

Figure 3. Kinetics of gas evolution.

Gas inclusions (air components, water, CO_2) that are the most loosely-bound with the surface of particles as well as argon adsorbed after completion of the electrical explosion, are removed at 100-150 °C along with the external particle shell formed in passivation. The next portion of gases chemically bounded to the surface is desorbed at 250-400 °C (Figure 3). The temperature of desorption finishing is about 400 °C.

Oxidation of powders in reactions with air and water

DTA and TG

Table 5 demonstrates the data of beginning of the oxidation temperature T_{onset} during DTA in air for different powders with the heating rate of 5 °C/min.

Table 5. Comparison of data of oxidation beginning temperature during DTA in air

Sample	Al, %	S_{BET}, m^2/g	D, nm	T_{onset}, °C
N_2/N_2	75.4	18.2	44.2	375
N_2/air	74.0	17.5	40.3	400
N_2/CO_2	70.7	21.0	40.4	425
N_2+CO_2/ N_2	60.8	34.3	32.4	397
CO_2/CO_2	16.4	38.0	30.8	400
Ar/air	79.8	16.7	54.6	420

It can be seen from Table 5 that T_{onset} is independent of powder fineness (size varies twice and purity varies almost 5 times). For all cases the temperature of oxidation beginning is practically the same: $T_{onset} = (400 \pm 25)$ °C.

It seems that the temperature of oxidation beginning corresponds to the finishing temperature of gases desorption. The two processes are connected with each other. Adsorbed and chemically bonded gases prevent particles from oxidation in air. Oxidation in water gives other results.

Oxidation in reaction with hot water

Correlation between conditions of nanopowder synthesis, the specific surface and chemical activity in reaction with hot water has been determined.

In this study, the temperature of reaction onset in independent experiments on evolution of the first hydrogen bubbles, a pH change, and some self-heating of the mixture was registered. Some results are presented in Table 6.

Table 6. Reaction with hot water

No.	Sample	S_{BET} of sample, m^2/g	Al content, %	pH, before/after reaction	S_{BET} of products, m^2/g
1	N_2/air	13	74.0	5.0/9.7	370
2	N_2+CO_2/ N_2	34.3	60.8	5.1/9.4	340
3	CO_2/CO_2	38	16.4	5.2/8.2	165

Table 6 shows that there exists a direct relation between the amount of active aluminium content and the specific surface of final product. An ultrafine aluminium oxyhydroxide with the specific surface $S_{BET} = 368$ m^2/g was produced by oxidation of nanosized aluminium by hot water.

Figure 4 demonstrates the hydrogen release during reaction with water at 60 °C.

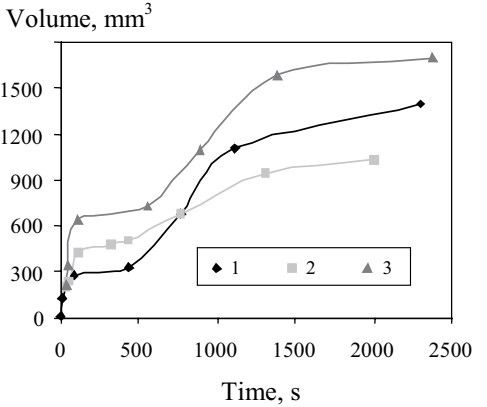

Figure 4. Kinetics of hydrogen realise in oxidation of Al samples 1, 2, 3 (Table 6).

It can be seen from Figure 4 that various types of Al nanopowders oxidized in two stages. TG analysis of final products shows the aluminum oxyhydroxide dehydration. This result allows to suppose that the reaction $\mathbf{2Al + 4H_2O \rightarrow 2Al\,OOH + 3H_2}$ is limitative for samples 1 and 2. As for sample 3, Table 6, alumina probably comes together with pseudo-boehmite in less alkaline medium (pH 8.2).

The oxidation level of Al powders in reaction with hot water (60 °C), % masses degree of oxidation, and the temperature of reactions onset, T °C, are given in Figure 5.

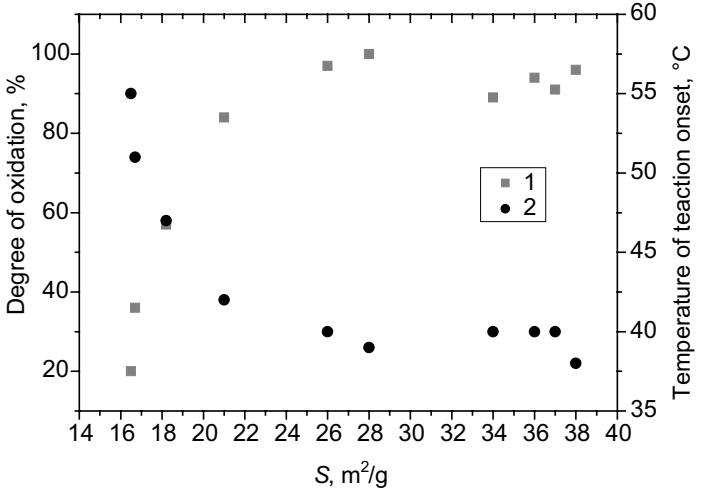

Figure 5. The degree of oxidation (1), % masses, and the temperature of reactions onset, T °C (2).

An oxidation level in reaction with water is from 36 to 100% for various types of powders and their specific surface.

The more active is the powder, the lower is the temperature of reaction onset with water and the higher is the oxidation degree at 60 °C. The experimental data on relative chemical activity show that the value of specific surface is the major characteristic of powder.

Combustion of nanoaluminum / gelled water compositions

Preface

The possibility of combustion of the nanoaluminum with water in the mode of a normal combustion regime has been established in the experimental work [6]. The calculated heat of combustion of the Al nanopowder stoichiometric mixture with water, recounting to the pure metal (50/50%), is 7570 kJ/kg thus attributing this system to high-energy material. Owing to inert admixtures in the powders, this value is vastly less (by 10-15%).

In the paper [5] the more detailed data on combustion of the stoichiometric aluminum mixture with water is given. In particular, the law of combustion rate of the stoichiometric mixture is*:* $U = 0.183\ (p/p_0)^{0.4}$, cm/s. Also the incompleteness of aluminum combustion is observed.

Report [8] shows, that, for using the aluminum/water mixture as propellant, the ratio of 40% Al/60% gelled water is preferable. In this case, the completeness of Al combustion reaches 100%. The combustion temperature and the combustion rate increase with increasing the oxidation degree. The combustion rate values under the pressure of 7 MPa for the aluminum concentrations from 38 to 57% are from 0.8 to 1.8 cm/s. The temperature of combustion reaches 2450 °K.

The present study is a continuation of [5-8], and we used the optimal ratio aluminum/water 40/60%.

The combustion rate

Figure 6 demonstrates clearly how the concentration and dispersivity of Al powder in Al/water slurry influence the combustion rate.

The first curve in Figure 6 shows the dependence of combustion rate on pressure for the sample of Ar/air having the specific surface of 16.7 m^2/g (Table 5), in the stoichiometric 50/50% composition of Al/gelled water.

Investigations confirmed the early-represented data [8] showing that aluminum decreasing in the composition of 40/60% increases the completeness of metal combustion and increases the combustion rate (curve 2). The sample of Al powders was the same – Ar/air.

Curve 3 also corresponds to the mixture of 40/60%, but the specific surface of nanoaluminum was of 34.3 m^2/g (sample N_2+CO_2/ N_2, Tables 1, 2, and 5). The combustion rate grew sufficiently and reached 2.4 cm/s under the pressure of 5-8 MPa.

It is important to point out that the dependence of combustion rate on pressure is very weak (line 3), the exponent in the combustion law $\nu = 0.12$, and is even independent of pressure in the area of 5-8 MPa. That area of pressure is the working range for propellants. Visual observation of burning surface and analysis of combustion products point to the facts that burning is more uniform and efficient, and solid products are less agglomerated consisting of nanosized corundum.

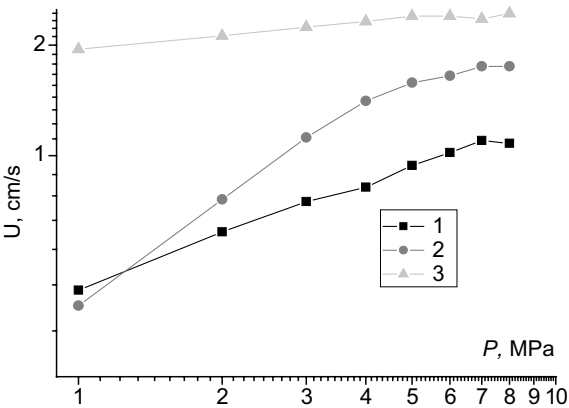

Figure 6. (1) – sample Ar/air, S_{BET}= 16.7 m^2/g, stoichiometric 50/50% composition, (2) – sample Ar/air, composition of 40/60% Al/water, (3) – sample N_2+CO_2/ N_2, S_{BET} =34.3 m^2/g, composition of 40/60% Al/water.

Conclusion

Because of peculiar chemical features of the Al nanopowders, the oxidation degree of the powder by water and the temperature of the reaction onset can be used as a criterion to compare chemical activity of the powders produced under various conditions.

Phase composition and phase structure of powders produced under different conditions of heating and environment are overwhelmingly important. Stability of phase constitution of particles as well as stability of their energetic and other

characteristics during storage time and their behavior under external influences are also sufficient.

Inorganic coatings allow producing powders having monocrystal nanosized particles.

Though pure metal content averages out to 75%, powders demonstrate high energetic activity in oxidation reactions due to high dispersivity of powders.

Compared to conventional Alex® [3], the specific surface of powder produced using justified engineering conditions is three times higher. This allowed sufficiently improving characteristics of gelled Al/water compositions, namely, the combustion rate became two times higher and less agglomeration has been observed.

Adsorbed and chemically bonded gases prevent particles from oxidation in air. The temperature of oxidation beginning corresponds to the finishing temperature of gases desorption. Oxidation in water gives other results.

An ultrafine aluminium oxyhydroxide with the specific surface $S_{BET} = 368\ m^2/g$ was produced by oxidation of nanosized aluminium by hot water. On the other hand, an oxidation with water in combustion regime allows producing nanosized corundum. It is important that the dependence of combustion rate on pressure is very weak, and is even independent of pressure in the area of 5-8 MPa.

It has been established that the combustion rate sufficiently grows when a high-dispersed powder is used.

In conclusion we can say that the exploding wire method is a very promising method of ultra-fine powders production. It is possible to produce ultra-fine powders with controlled phase compositions.

Real future success requires the coordinated joint efforts of a wide circle of researchers and technologists, producers and users.

Acknowledgment

Financial supports from the INTAS (grant 03-53-5203), INTAS-SB RAS (grant № 06-1000013-8949), and from the Federal Task Program (State Contract 02.513.11.3127) are acknowledged.

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