

Application of Nanodispersed Powders Produced by Wire Electrical Explosion Method

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Abstract In the present work some properties of nanopowders and possible areas of their applications are discussed. Main attention is paid to the use of nanodispersed powders (NDP) in new materials production technologies.

Keywords : Nanodispersed powders, Wire electric explosion

1. Introduction

Nanodispersed powders (NDP), due to their specific properties, are more and more widely used as basic materials for the production of ceramics and composites, superconductors, solar batteries, radio absorption covers, filter, getters, lubricant additives, colouring and magnetic pigments, components of low-temperature solder alloys etc. As an amount of fundamental and applied research on NDP grows, this list is rapidly increased. Many of NDP applications have already been realized. Some other applications are on the development stage, but the major part of possible NDP applications still remains unexplored. There is a number of economically perspective way for NDP to use in production of other materials, which are of practical interest for today.

In the present work we are trying to analyze our results and experience of works with NDP produced with wire electrical explosion (WEE) technology¹⁻⁵⁾ and to consider these new applications.

2. Combustion of Aluminum in Nitrogen (Aluminum Nitride Synthesis)

A large amount of aluminum nitride has been found in the products of aluminum combustion in air. This unexpected result made us more carefully study the process of aluminum combustion in nitrogen in order to get NDP of aluminum nitride.

Presented below are the results of studies of the alu-

minum nitride formation when nitriding ultradispersed aluminum UDA-V, obtained with the electric explosion technology. The synthesis was made in a reactor in the medium of pure and technical nitrogen and a pressure of (0.01–1.2) MPa. In some experiments oxygen was added to nitrogen.

UDA-V powder was placed to the quartz capsule and then fired using tungsten spiral, heated with electric current. The temperature of the combustion wave was measured with tungsten-rhenium thermocouple. The temperature profile was recorded with an oscilloscope. The content of condensed products of the combustion was analyzed with chemical and X-ray analysis. The gas medium was controlled with a chromatograph. The results were compared with those of the industrial powder ASD-4. The main physico-chemical properties of aluminum powders used in the experiments are shown in Table 1.

It was found that highly dispersed aluminum steadily burns in nitrogen and in nitrogen-oxygen mixtures at room temperature and atmospheric pressure. After the ignition the combustion wave propagated over the

Table 1. Properties of nanopowders investigated in this study

Physico-chemical properties	UDA-V	ASD-4
Shape of particle	sphere	sphere
Average size of particle, μm	0.23	10
Specific surface area, m^2/g	0.8	0.15
Active metal content, %	95	99.50

sample. Depending on the conditions of the experiment, the rate of combustion changed within the limits of (2–8) mm/s. Maximum temperature on the wave front of the combustion reached 2200°C. The products of nitridation are loose light-gray powder.

During the nitriding reaction in the medium of pure and technical nitrogen with atmospheric pressure, the content of AlN was nearly constant - about 87 wt.%. With above one atmosphere it was 89.9 wt.%. The pressure increase to two atm leads to the decrease of AlN output. When increasing the pressure of nitrogen, the content of free aluminum increases. The degree of coagulation of nitriding products also increases, which is proved by sharp decrease of their specific surface area.

The tests of diluting the pure nitrogen with oxygen showed that at a concentration of oxygen in the mixture up to 2 vol.% the amount of aluminum oxides formed as a result of reaction did not considerably change, but the output of AlN increased.

Further increase of oxygen content in the reaction mixture lead to the reduction of the output for AlN and the increase of the part of aluminum oxides. In all of the experiments the presence of non-reacted metal did not exceed 5 wt.%. Table 2 shows the experimental results.

High reactivity of ultradispersed aluminum allows to obtain aluminum nitride in the combustion mode with an output of (90–91) wt.% which is nearly equal to the content of active metal in the input powder.

The behavior of coarsely dispersed powder ASD-4

in the nitriding experiments is different from that of UDA-V. Ignition of the ASD-4 powder was possible only in the medium containing more than 10 vol.% of oxygen. As it was expected before, the major part of the condensed combustion products was the non-reacted aluminum and its oxides. Aluminum nitride was not found in the reaction products.

In order to activate the nitriding reaction of the coarsely dispersed aluminum powder, UDA-V was used. The results of the experiments exceeded all expectations. With the concentration of UDA-V 10 wt.% and higher, binary mixture of the powders can be easily ignited and shows stable combustion in technical nitrogen at normal conditions. The aluminum nitride output reaches 97 wt.% in the combustion mode (see Table 3)

Aluminum oxides are formed in small amount and do not appear at all. The content of non-reacted aluminum stays about the same level of (2–5) wt. %.

With the less than 10 wt.% concentration of UDA-V in the initial mixture, the samples are hard to ignite and burn with attenuation. The stable combustion of the mixtures occurs at increased pressure in the working volume, but the specific surface of the aluminum powder also decreases.

3. Production of Ultradispersed Molybdenum Disulfide (MoS₂)

The most interesting for practical applications is the

Table 2. Influence of the gas medium on the content of UDA-V combustion products. pressure 0.1 MPa

Medium composition (vol.%)		Phase content of combustion products of aluminum in nitrogen (wt. %)				Specific surface area of the combustion products, m ² /g
N ₂ tech.	O ₂	AlN	γ-Al ₂ O ₃	α-Al ₂ O ₃	Al ⁰	
99.5	0.5	89.8	5.8	–	4.4	6.2
99.0	1.0	90.0	6.5	–	3.5	5.9
98.0	2.0	89.7	7.1	–	3.2	5.7
95.0	5.0	87.5	8.8	0.8	2.9	5.7
90.0	10.0	83.3	11.1	2.5	3.1	3.9

Table 3. Influence of UDA-V addition on nitriding of ASD-4 powder. Technical nitrogen, pressure 0.1 MPa

Powders medium composition (wt.%)		Phase content of the reaction products (wt.%)			Specific surface (m ² /g)
UDA-V	ASD-4	AlN	Al ₂ O ₃	Al ⁰	
100	0	98.8	5.8	4.4	6.0
50	50	94.9	2.1	3.0	4.31
30	70	95.5	1.7	2.8	2.58
25	75	95.6	1.5	2.9	2.32
10	90	96.8	trace	3.0	2.02

production of ultradispersed MoS₂, using self-propagating high-temperature synthesis (SHS). MoS₂ is a self-lubricating material used as a component of highly effective lubricants. The ultradispersed state of MoS₂ improves the properties and sedimentation stability of the lubricants.

Calculated heat of stoichiometric reaction of molybdenum and sulfur (60% Mo and 40% sulfur) is 411 cal/g., which is enough to conduct the synthesis in the combustion mode (SHS). The starting molybdenum is in ultradispersed state, sulfur when burning is in liquid and gas state. Hence it reacts with the particles of molybdenum on the molecular level and the size of the particles of reaction products should be determined by the size and structure of the starting molybdenum particles. To keep the product in the ultradispersed state it is necessary that the maximum temperature of the combustion should not exceed the melting temperature of MoS₂ (2380 K).

The major task of the research in this case is to define the optimal technological parameters of the synthesis - density of the starting mixture, chamber pressure, ratio of the components, and diameter of the sample. Pilot experiments with stoichiometric mixtures pressed to tablets of 10 mm diameter and 20 mm height showed that at low densities the process proceeds with highly incomplete transformation due to the sulfur boiling away and transfer of the part of sulfur from the reaction zone. At high density the process is hardly initiated due to intense heat removal. The optimal relative density was 0.75–0.8.

The synthesis of molybdenum disulfide was carried out in the constant argon pressure of (0.1–7) MPa. The process rate was determined with a streak camera; combustion temperature was measured with tungsten-rhenium thermocouple recording with C9-6 oscilloscope. The transformation ratio of the input mixture to the output product was determined via changes in the sample mass after the synthesis, and parallel, the sulfur content was checked with chemical analysis. Besides, the synthesis products were studied with the method of X-ray phase analysis.

Characteristic temperature oscillogram for the synthesis of molybdenum disulfide given in Fig. 1 shows a multistage character of the process. During the propagation of the synthesis wave the temperature «step» is practically coincident with boiling temperature of sulfur at a given pressure, which increases from 777 to

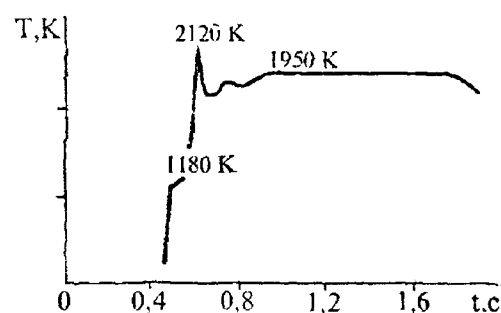


Fig. 1. Temperature change as a function of time during SHS process of MoS₂.

1190 K in the pressure interval of (0.1–7) MPa. This means that during the propagation of the synthesis wave determining the process kinetics, a reaction of molybdenum with sulfur melt takes place at the boiling temperature of sulfur with the formation of a primary film of the product on the particles of molybdenum. The efficiency of transformation calculated with an independent thermodynamic method, taking sulfur boiling temperatures at different pressures, does not exceed 45%. Formation of the major part of molybdenum disulfide is observed in the high-temperature after-reaction zone, which corresponds to a long «plateau» with a temperature of (1950–1980) K on all the oscillograms.

When increasing pressure, the maximum temperature of synthesis increases and reaches 2180 K at a pressure of 7 MPa. Simultaneously a relationship between temperature and transformation efficiency (final product output) is observed. When increasing pressure, the output of molybdenum disulfide also grows, but significantly slower than it was expected.

Since in the zone of liquid sulfur just a small part of the product is formed and the output is mainly produced in the after-reaction zone reacting with the sulfur vapor, the incompleteness of transformation is the most probably connected with partial removal of sulfur vapor from the sample.

Thus, the increase of product output can be realized by two ways: further increase of pressure and combustion temperature or sulfur content in the input mixture more than stoichiometry to compensate sulfur vapor loss.

The first method is not technological since it requires high pressures (it is estimated to 20 MPa) and besides it can lead to exceeding the MoS₂ melting temperature and formation of monolith disulfide sam-

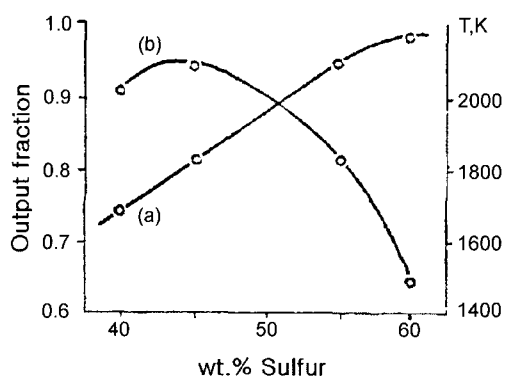


Fig. 2. Change in output fraction (a) and combustion temperature (b) in SHS process of MoS_2 as a function of Sulfur content.

ple due to significant temperature increase, which cannot lead to the formation of nanosized MoS_2 . The second method (Fig. 2) allows to obtain 99% output of MoS_2 even at a pressure of 4 MPa and sulfur content of 60 wt.% despite the process temperature and rate decrease (1).

The increase of sample diameter up to 30 mm and tight insertion of it into an aluminum or steel barrel prevent sulfur removal through the lateral surface of the sample and provide its complete reaction with molybdenum that allows to get the output of molybdenum disulfide of 99.5% at a pressure of 2 MPa.

X-ray phase and chemical analyses prove that the product of the synthesis is nearly pure molybdenum disulfide. The change of the specific surface area of the obtained product shows that its dispersity is 2–3 times higher than the dispersity of the input molybdenum and equals to $(17–20) \text{ m}^2/\text{g}$.

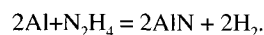
Apparently, the use of this method can result in the formation of a number of other compounds in form of ultradispersed powders including oxides, carbides, nitrides etc.

4. Production of Hot Hydrogen with Aluminum NDP

Compact hydrogen generators are being used in different fields of modern technology. For some applications, for example, in laser technology, hydrogen heated to relatively high temperatures is required for some types of welding. Common pyrotechnic hydrogen generators do not use aluminum due to high stability of common aluminum powders

to oxidation, even though aluminum is considered to be the most prospective metal for the compounds of this type.

Experiments using aluminum NDP have shown that it is possible to obtain the reaction of the aluminum NDP in the combustion mode with a number of substances generating considerable amounts of hydrogen. The major interest is connected with the reactions of the aluminum NDP with hydrazine (N_2H_4), which is capable of exothermic decomposition producing a mixture of hydrogen and nitrogen. The aluminum NDP, due to its high chemical activity, allows to bound nitrogen to aluminum nitride with additional heat evolution. For stoichiometric mixture (63% of aluminum) the calculated temperature of combustion is 3290 K and the calculated combustion heat reaches 1909 cal/g. The process of interaction goes according to the equation:



With stoichiometric relation of the components, 520 cm^3 of pure hydrogen per gram of the input mixture should be generated with heat evolution (7.99 kJ/gram of mixture).

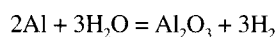
Common aluminum powders do not react with hydrazine even at high temperatures. The use of the aluminum NDP and densification of hydrazine with small (1–3%) polymer additives leads to a reaction in combustion mode even at pressures of 1 MPa. The output of hydrogen in this case depends on the ratio of components and active metal content in the input NDP of aluminum. With the aluminum content lower than stoichiometric (hydrazine excess) the mixture of hydrogen and nitrogen is formed, however the total gas evolution increases up to $(1500–2000) \text{ cm}^3/\text{gram}$ of mixture. In the case of use of NDP with high content of adsorbed water and air (low content of active metal in the NDP) the gas products contain considerable amount of water and in the condensed surplus not only aluminum nitride, but aluminum oxide is also found (up to 12%).

Another unusual property of the aluminum NDP is the capacity to react with water in gel-state (thickened with polymer additives) in the combustion mode. Up to now the reaction of aluminum oxidation with water was possible to obtain with rather low completeness of transformation and only at temperatures about 2000 K. The aluminum is inert towards water even at high boiling temperatures (high pressures). Our experi-

ments with the aluminum NDP and water thickened with polymer additives have shown that the combustion of this system is possible even at atmospheric pressure. With stoichiometric content of aluminum (50%) during the combustion 622 cm³ of hydrogen per gram of mixture is generated. The heat of the combustion reaches 1810 cal/g, and calculated adiabatic temperature of the combustion - 3400 K.

The reactions of NDPs with alcohol (methanol, ethanol, propanol etc.) in the combustion mode are considered even more prospective. In this case one can expect the hydrogen generation from 600 to 1250 cm³/g, and heat of the mixtures combustion (not counting after-burning of hydrogen and carbon) can be from 1050 to 1660 cal/g. The major problem of the realization of these reactions is to select proper thickeners providing the overheat of the condensed phase up to the temperatures of «NDP activation» - (300–400)°C, the temperatures at which NDP liberates its stored excessive energy and shows the biggest chemical activity.

Another aspect of the reaction of aluminum NDP with water in the combustion mode is the possibility to obtain monolith aluminum oxide as a result of the reaction



Formation of Al₂O₃ monolith product possessing the properties of corundum was observed in our experiments at the pressure of 3–5 MPa. Adding of small (about 0.5–1%) additives of soluble salts of chrome, nickel, copper to water, or use of metallic additives to the aluminum NDP give the opportunity to produce technical corundum with the properties of semiprecious stones (technical ruby, sapphire, emerald etc.).

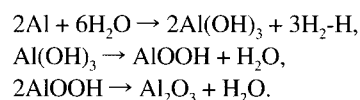
5. Interaction of Aluminum NDP with Water

Newly made fresh powders of aluminum react intensely with «liquid water» liberating a large amount of heat. Passivated powders react, however, only after an induction period which depends on the oxidation degree of a powder.

The reaction kinetics was studied by hydrogen liberation with volume measuring and gas chromatography methods. In the experiments a glass reactor with a magnetic mixer, twice-distilled water and 0.1–0.02 g of the powder were used.

It was found that the aluminum NDP produced with

the method of electric explosion is subjected to high transformation ratios up to 1. The phase content of the reaction products was studied with x-ray phase and thermal analyses. Crystalline bayerite Al(OH)₃, pseudo-boehmite AlOOH and amorphous aluminum oxide were found. With the experiment temperature T_{EXP} increase, the content of Al(OH)₃ and AlOOH decreases and the content of the amorphous oxide increases. At T_{EXP} higher than the threshold temperature Al(OH)₃ and AlOOH content decreases and the content of the amorphous oxide grows. At T_{EXP} higher than the threshold temperature Al(OH)₃ is not found in the reaction products and the main product is the amorphous oxide with AlOOH admixture. The formation of highly dispersed aluminum oxide proceeds according to:



During oxidation the specific surface area increases by an order or more. The final values of S_{SPEC} reach 100–450 m²/g and depend on the dispersion of the powder and T_{EXP}. The latter dependence has the experimental type.

The formed aluminum oxide has two-dimensional structure in a needlelike form of (20÷10) nm diameter, going from the denser nucleus of particles (see Fig. 3). Further heating of the products up to 780 K leads to 10–15% increase of their specific surface.

This oxide may find an application as an adsorbent in biotechnology and medical industry as a carrier of different catalysts it is also possible than this material can be used in ceramic manufacturing of the most important details.



Fig. 3. Transmission Electron Micrographs of Al₂O₃ particles produced by oxidation of Al NDP with water.

6. Conclusion

Electric explosion method of NDP production is a new prospective technological process providing the production of NDPs with a set of new properties.

Technologies using the electric-explosion NDPs of metals allow to get a wide range of products with unique properties and to realize the reactions, which are impossible to accomplish with common metal powders.

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References

1. N. A. Yavorovsky, Yu. A. Kotov, *Fizika I Khimia Obrabotki Materialov: Physics and Chemistry of Material Processing*, (1978) 24. (In Russian)
2. G. V. Ivanov, N. A. Yavorovsky, Yu. A. Kotov *et al.*: DAN SSSR, Reports of the USSR Science Academy, **275** (1984) 873. (in Russian)
3. N. A. Yavorovsky: *Izvestiya Vuzov, Fizika, News of High School*, (1996) 114.
4. N. A. Yavorovsky, V. G. Domashenko, P. V. Balukhtin: *KORUS 2000, Part 3*, (2000) 273.
5. A. P. Liashko, G. G. Saveliev, N. A. Yavorovsky *et al.*: *React. Kinet. Catal. Lett.*, **37** (1998) 139.