

Nanopowders produced by electrical explosion of wires

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Abstract

Electrical explosion of wires (EEW) is a method for production of nanopowders. Depending on type of chemical composition of working ambient in the discharge chamber nanopowders of carbides can be produced (EEW in hydrocarbons) or nanopowders of oxides (EEW in oxygen contained medium). Phase compositions of nanopowders prepared by electrical explosion of tungsten and aluminium wires in liquid and solid hydrocarbons and water were investigated. The influence of the electrical parameters and the reaction ambient characteristics on the phase and size composition of EEW products was studied.

Some fields of application of electroexplosive nanopowder are discussed. It is improvement of the tribological characteristics of industrial oil after treatment with electrical explosion of copper wires, which causes a friction constant to be decreased to 40 %. Very active oxide-hydroxide phases can be used for water purification from ions of heavy and radioactive metals.

Keywords: electrical explosion of wires, nanopowder, carbides, oxides

1. Introduction

Nanosized powders due to their specific properties are more and more widely used as basic materials for production of ceramics and composites, filters, lubricant additives, for solution of ecological problems as catalysts, sorbents, etc.

One of the ways of nanopowder production is electrical explosion of wires (EEW). It is a process of explosive destruction of a metal wire under the action of great density current ($>10^6$ A/cm²) [1]. EEW is characterized by the following peculiarities: time of explosion is $10^{-5} \dots 10^{-8}$ s; temperature at the moment of explosion can reach the value more than 10^4 K, pressure $\sim 10^9$ Pa; velocity of product recession is from 1 to 5 km/s. Material of the wire transmutes into particles of nanosized range (10...100 nm) in accordance with certain conditions. Extremely nonequilibrium conditions of EEW cause some unusual properties of nanopowders.

Electroexplosive nanopowders have as a rule the spherical form of particles, they are steady against oxidation and sintering at room temperature and characterized with high diffusion activity at the heating. The threemodal particle size distribution is formed under the process of EEW. Dispersed composition is one of the most important parameters that determine their technical characteristics (packed density, flow rate, slope angle, and others), and, hence, their range of use.

The dispersed composition and other characteristics of nanopowders depend on all conditions of explosion – firstly, on the electrical parameters (energy consumed by wire before explosion, energy of arc stage, the velocity of energy input or power density. The nature of wire metal and its geometry (length and diameter of wire), microstructure and substructure of wire metal, environmental properties – pressure and kind of gas, introduction of chemically active gases in inert gas also have influence on the dispersiveness and other properties of nanopowders.

An important advantage of EEW technology is the adjustability of properties of EEW products by means of electrical parameters. Low energy consumption (< 10 kWh/kg) is due to direct heating of wire by electric current without heat carriers and due to high heating rate ($> 10^7$ K/s) that provides adiabatic conditions of energy transmission to wire. Yield of nanopowders on the basis of aluminum is 50 g/h, on the basis of tungsten – 300 g/h under production using one set. This technology is environmentally benign one: the process of nanopowder production is carried out in closed chamber, there is no technological emission.

EEW in inert gases or hydrogen is used to produce powders of metals, alloys, and intermetallic compounds. EEW in chemically active ambient is used to produce nanopowders of chemical compounds of metals: oxides, nitrides, carbides, etc.

The metal carbides such as Al_4C_3 , LaC_2 , TiC , ZrC , NbC , Nb_2C , Ta_2C , MoC , and W_2C were synthesized by electrical explosions of corresponding wires in ethane, isobutene, acetylene, and mixture of acetylene-argon [2-4]. Aluminium oxides were obtained by electrical explosions of aluminium wires in air and in oxygen-argon mixture [5, 6]. From [2-4] it follows that EEW in gaseous hydrocarbons results in obtaining carbides deficient in carbon (W_2C , WC_{1-x} , and Ta_2C). Main product of aluminium EEW in gas containing oxygen is low-temperature crystal modification $\gamma-Al_2O_3$ [5, 6].

To increase the output of chemical compounds and to prepare carbon-saturated phases and high-temperature oxides phases, it is expedient to increase the pressure in the discharge chamber, which is not always justified technically, or to use condensed medium. The density of reactants is much higher during wire explosions in condensed medium compared to explosions in gases. This fact allows the chemical compounds output to be increased and their phase composition to be changed. Peculiarities of EEW process in condensed medium allow the technological capabilities of the electroexplosive method of obtaining nanopowders to be extended.

In this paper the phase and chemical compositions of nanopowders produced by electrical explosion of wires in liquid and solid hydrocarbons and water are presented. The fields of application of electroexplosive nanopowder are shown.

2. Experimental details

The principal scheme of the experimental installation for producing electroexplosive powders is shown in the Figure 1. The installation works as follows. The capacitor battery 2 is charged from the high-voltage power source 1. The wire driving mechanism 3 is used for automatic feed of the exploding length of wire 4 in the electrodes gap. When the wire reaches the high-voltage electrode 5, the commutator 6 operates, and the electric discharge of the capacitor battery occurs on this length of wire – the wire explodes. Obtained powder collects in the powder collector 7. Gas refined from powder is given back in the explosive chamber 9 by means of the ventilator 8. The explosive chamber 9 is vacuumed before working, and then the chamber is filled with working gas atmosphere by means of system 10. A special discharge chamber for carrying out the explosions in liquid ambient was developed [7].

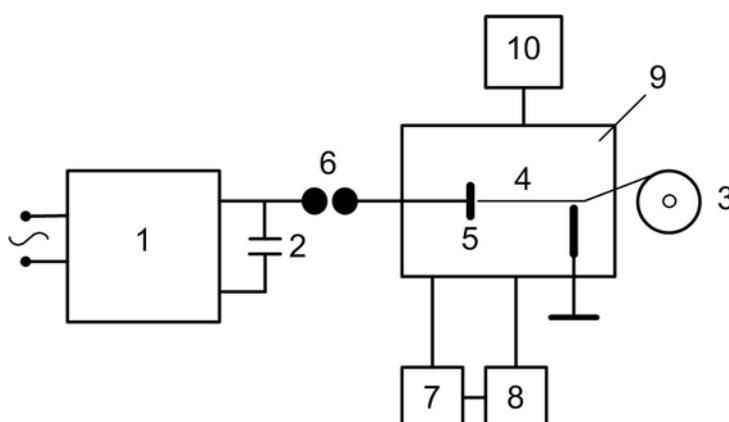


Figure 1. Principle Scheme of Experimental Setup: 1 - high-voltage power source, 2 - capacitor battery, 3 - wire supply unit, 4 - exploding wire, 5 - high-voltage electrode, 6 – commutator, 7 - powder collector, 8 – ventilator, 9 – explosion chamber, 10 – gas filling system

The tungsten and aluminium wires with diameter $d = 0.2...0.3$ mm and length $l = 40...200$ mm were used in the experiments. Electrical explosion of wires was carried out under conditions of “fast” explosion with an arc stage or with infinite current pause when almost all accumulated in capacitor energy was consumed by wire before explosion. Energy parameters of EEW were regulated with change of charging voltage and geometric characteristics of exploding wires. The specific electrical energy input in the wire (e) was changed from 0.4 to $1.8e_s$ (e_s is the sublimation energy of the wire material); the energy of the arc stage (e_a) – $(0.7...1.7)e_s$.

Parameters of electric circuit: capacitance $C = 2.25 \mu\text{F}$; charging voltage $U = 15 \dots 30 \text{ kV}$; inductivity $L = 0.58 \mu\text{H}$.

The phase analysis of the obtained powder was performed using $\text{CuK}\alpha$ -radiation of a DRON-3.0 X-ray diffractometer. Particle shapes and the dispersiveness were determined by means of a JSM-840 scanning electron microscope. The determination of specific surface area (S_{sp}) was carried out by using a method of low temperature nitrogen adsorption (BET). The differential-thermal analysis (DTA) and thermogravimetric analysis (TGA) was performed with apparatus Q-1000. The method of radiation probing (electron paramagnetic resonance) was used for quantitative determination of aluminium oxide-hydroxide phases in product of EEW.

3. Results and discussions

According to the X-ray data, powders prepared by EEW in hydrocarbons contain the carbides phases and residual metal (5...10 %). Phase compositions of nanopowders prepared by electrical explosion of tungsten and aluminium wires in liquid hydrocarbons (C_6H_6 , C_6H_{14} , $\text{C}_6\text{H}_5\text{CH}_3$, and $\text{C}_{10}\text{H}_{22}$) and solid paraffin are shown in the Table 1.

Table 1. Phase Composition of Powders Prepared by Electrical Explosion of Tungsten, Titanium and Aluminium Wires

Material of the wire being exploded	Surrounding ambient of the EEW	Phase composition of the EEW products
W	Hexane	W, W_2C , WC_{1-x}
W	Decane	WC_{1-x} , W_2C , W
W	Benzene	WC_{1-x} , W_2C , W
W	Toluene	WC_{1-x} , W_2C , W
W	Paraffin	WC, W
Al	Decane	Al, Al_4C_3

The main product of the tungsten EEW in decane $\text{C}_{10}\text{H}_{22}$ is carbide WC_{1-x} in contrast to the product of EEW in gaseous hydrocarbon – W_2C [4]. High temperatures during tungsten carbide synthesis by EEW and fast cooling of the prepared powders lead to stabilization of the metastable disordered state of carbide (WC_{1-x}).

The output of carbon-saturated carbide phases (WC, WC_{1-x}) increases with rise of the working medium density as well as elemental composition of hydrocarbons (C/H ratio in hydrocarbon molecules) and the value of the consumed energy. Figure 2 shows the qualitative composition of the tungsten EEW products for the indicated liquid hydrocarbon types and a deposited energy of $\sim 1.2e_s$.

It can be seen from the Figure 2 that the tungsten carbide WC_{1-x} output increases upon increasing the C/H ratio and the liquid hydrocarbon density, whereas the metal tungsten content in the products decreases. However, even for the maximum

consumed energy ($e/e_s = 1.2$), tungsten carbide remains the nonstoichiometric compound WC_{1-x} deficient in carbon. According to the X-ray data (Table 1), tungsten EEW in saturated solid hydrocarbon – paraffin – allows stoichiometric carbon-saturated tungsten carbide WC to be prepared.

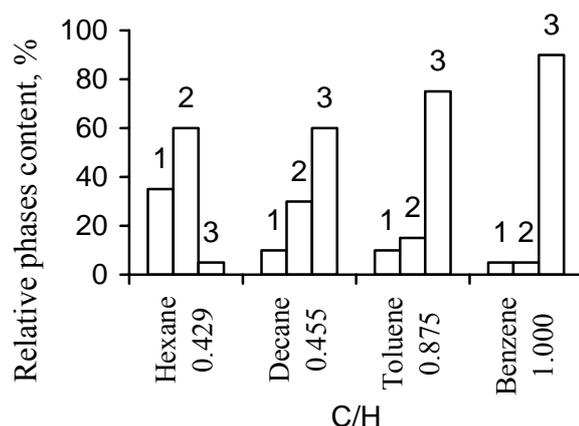


Figure 2. Relative contents of W (1), W_2C (2), and WC_{1-x} phases (3) in tungsten EEW products having different C/H ratios

The comparison between the formation of aluminium and tungsten carbides by EEW showed that the output of the chemical compounds depends on their thermal stability: the more thermally stable they are, the higher their output [7].

The main product of aluminium EEW in decane is unreacted aluminium even at sufficiently high level of consumed energy ($e/e_s = 1.5$). The relative content of aluminium carbide did not exceed 40 %. The temperature at which aluminium carbide remains stable is limited to temperature lower than 3000 K. The chemical reaction takes place in the process of cooling after explosion due to diffusion of carbon atoms into the aluminium particle at temperature below the boiling point of aluminium (2720 K). In this reaction a solid carbide layer is formed on the metal particle surface, thereby limiting the diffusion of carbon atoms into the metal. The maximum temperature at which tungsten carbides remain stable is much higher than that for the aluminium ones. The spherical particles of tungsten carbides have smooth surfaces. The tungsten carbides are formed at temperature exceeding their melting point through the diffusion of carbon atoms into the liquid tungsten particle with formation of liquid tungsten carbide. Thus, the higher output of tungsten carbide nanopowders is a consequence of their higher thermal stability relative to those of aluminium carbides.

One of the applications of electroexplosive nanopowder is their use as the additives in lubricating oil for improving the tribological characteristics and increasing the wear-resistance of the machine parts. For example, copper nanopowder and fullerenes can

be used as such additives. The tribological characteristics of industrial oil after treatment with electrical explosion of copper wires were studied. The copper wires with diameter $d = 0.2$ and length $l = 50 \dots 120$ mm were used in experiments. The specific electrical energy input in the wire was $1.2e_s$. Suspension of copper nanopowder with concentration 0.05 mass.% was obtained in result of the treatment. To obtain suspension of carbon clusters (fullerenes) copper nanopowder were separated from oil with special centrifuge. The dependences of friction constant on load for initial mineral oil, oil contained copper nanopowder, and oil contained carbon clusters are shown in the Figure 3. Decrease of friction constant occurred to 40 %, if the oil contained copper nanopowder and the oil contained carbon clusters were used.

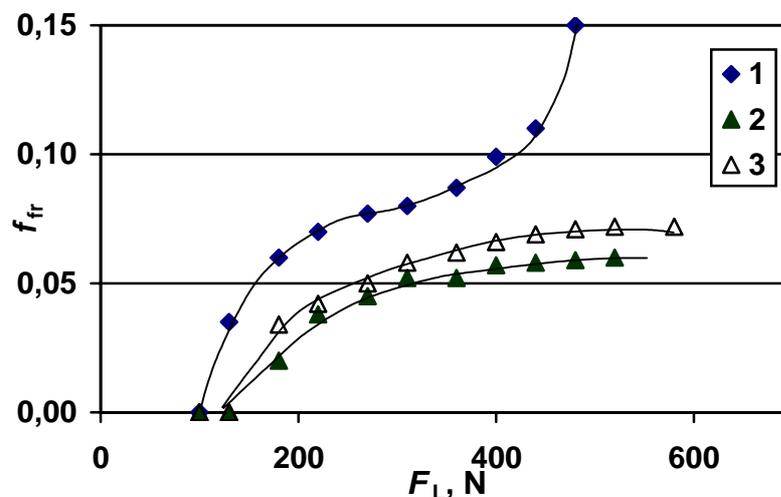


Figure 3. Dependences of friction constant on load for initial mineral oil (1), oil contained copper nanopowder (2), and oil contained carbon clusters (3)

Nanopowders produced by electrical explosion of aluminium wires in water are different crystal modifications of aluminium oxides: $\text{Al}(\text{OH})_3$, $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$.

According to the X-ray data, the main product formed by the electrical explosion of the aluminium wire in water is low-temperature modification $\gamma\text{-Al}_2\text{O}_3$. A content of residual aluminium decreases with the rise of energy consumed by wire and is about 15 % at $e_a/e_s > 1.5$. Dependence of abundance of residual aluminium Al^0 и $\gamma\text{-Al}_2\text{O}_3$ in the EEW products is shown in the Figure 4. A drastic decrease of residual aluminium is observed in the range $e/e_s \sim 0.9 \dots 1.1$. Similar dependencies were discovered previously by the investigation of EEW in gases [4-6]. Formation of size composition is the result of two mechanisms: dispersion of liquid metal and condensation of vapor phase. A metal part transforms to vapor phase rises sharply at $e/e_s > 1.0$. Electrical explosion of aluminium wires in water at $e/e_s = 1.0$ and arc stage ($e_a/e_s = 1.3$) results in complete oxidation of metal to $\gamma\text{-Al}_2\text{O}_3$.

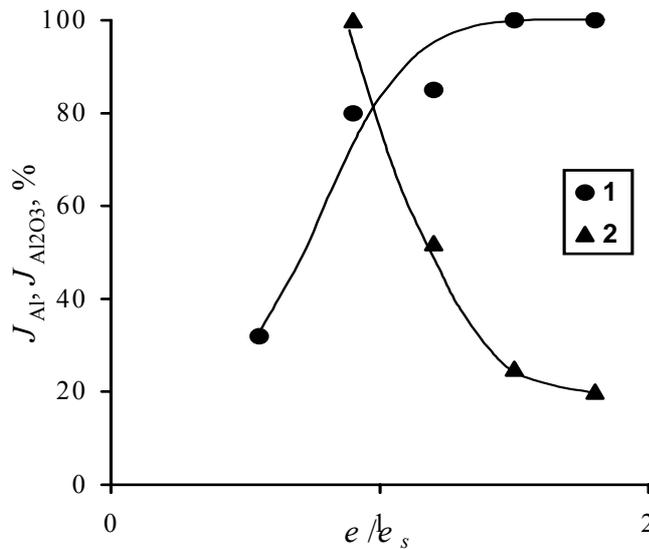


Figure 4. Dependence of the 100 %-X-ray diffraction patterns intensities on the energy input in the wire: γ - Al_2O_3 (1) and Al^0 (2)

Content of aluminium oxide and aluminium hydroxide in the product of EEW was determined using the method of radiation probing (electron paramagnetic resonance). The results are presented in the Table 2. These experimental data were tested by thermogravimetric analysis. The mass decrease at the heating the EEW products to 950 °C due to removal of sorbate water and fixed water was 2 and 5.3 % for the sample produced at $e/e_s = 1.2$; 2.3 and 17 % – for the sample produced at $e/e_s = 0.5$.

Table 2. Aluminium oxide and hydroxide content in the products of wires electrical explosion in water

№	e/e_s	Ratio oxide-hydroxide phases, %	
		Al_2O_3	$\text{Al}(\text{OH})_3$
1	0,6	25%	75%
2	1,20	80%	20%

The measured specific surface area S_{sp} of the aluminium oxide powder sample produced by EEW in water at $e/e_s = 1.5$ was 36.3 m^2/g . The average surface particle diameter calculated for this value of S_{sp} was 33 nm.

Unlike gas, liquid water is more dense ambient, which causes the formation of larger particles compared to explosions in gases. To increase the dispersiveness of aluminium oxide powder the electrical explosion of aluminium wires was carried out in inert gas argon above the water surface (Figure 5). The reaction chamber was vacuumed before the experiment and the filled with argon. The value of energy input in the wire was $0.9e_s$. Aluminium wire with a length 100 mm was placed at 30 mm above the water surface. According to the X-ray data, in this case the low-temperature modification γ - Al_2O_3 is formed as well. However, EEW in the protective gas

atmosphere above the water surface results in a decrease of residual aluminium content to 5...10 %. The maximum of the particle size distribution is shifted toward nanosized particles. The concentration of agglomerated particles that worsen the nanopowder quality decreases significantly. The hot unpassivated aluminium particles having no time to coagulate could interact with water producing highly dispersed aluminium oxide and gaseous hydrogen. After heating of the sample in air at 800 °C, S_{sp} increased to 146.3 m²/g, and the average surface particle diameter was 11 nm.

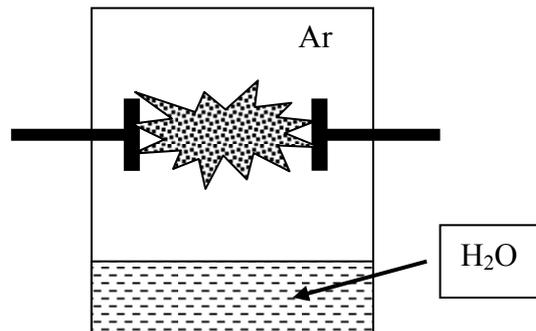


Figure 5. Scheme of experiment

Electrical explosion of wires in solid ice in contrast to liquid water leads to the rise of pressure in the discharge channel and temperature in chemical reaction zone. This fact results in formation of high-temperature modification of aluminium oxide. According to the X-ray data, it was obtained high-temperature modification of γ -Al₂O₃ and α -Al₂O₃ depending on mould stiffness containing air.

Very active oxide-hydroxide phases can be used for water purification from ions of heavy and radioactive metals. The possibility of purification from chrome and copper ions was studied [7]. Aluminium EEW was carried out directly in model solution. The specific electrical energy input in the wire was 0.9e_s. In this case the main product of aluminium EEW, as it was shown earlier, is Al(OH)₃. The results of experiments are shown in the Table 3.

Table 3. Dependence of impurities removal on the concentration of aluminium

Initial concentration of metals in water, mg/l		Concentration of aluminium, mg/l	Residual concentration of pollution, mg/l	
Cr	Cu		Cr	Cu
1,00	5,00	20	0,70	0,90
1,00	5,00	30	0,20	0,60
1,00	5,00	50	0,03	0,05
1,00	5,00	150	0,00	0,00

The residual content of chrome and copper ions in water was determined by photocolometric method. Practically total purification from pollutants ions is achieved when input amount of aluminium is 50...150 mg/l.

Another perspective application of aluminium EEW in water is production of hydrogen which is a reaction product of interaction of aluminium particles with working ambient components. The transformation ratio approaches 100 % without special additives.

4. Conclusions

Phase and size compositions of nanopowders prepared by electrical explosion of tungsten and aluminium wires in water and hydrocarbons were investigated. Control factors were electrical parameters, characteristics of wires, density of surrounding ambiances (hydrocarbons and water as gas, liquid, solid).

EEW in condensed ambient results in formation of high-temperature modification of chemical compounds (α -Al₂O₃) and increasing the output of carbon-saturated carbide phases (WC, WC_{1-x}) in comparison with explosions in gases. The content of carbide phases depends on the values of the upper warm-up border of chemical compounds stability.

The main product of aluminium EEW in water at the energy input in the wire $\sim 0.6...0.9e_s$ is Al(OH)₃. The rise of energy input in the wire to $1.8e_s$ leads to formation of low-temperature modification γ -Al₂O₃. The electric explosion in ice results in obtaining high-temperature modification γ -Al₂O₃ and α -Al₂O₃. The electrical explosion of aluminium wires in the protective gas ambient above the water surface leads to the formation of highly dispersed low-temperature modification γ -Al₂O₃ powder with the specific surface area up to 200 m²/g.

The tribological characteristics of industrial oil after treatment with electrical explosion of copper wires were studied. Copper nanopowder and carbon clusters (fullerenes) were obtained in result of EEW. Decrease of friction constant occurred to 40 %.

The possibility of water purification from heavy metals and other impurities was shown.

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