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Effect of Electrical Parameters and Surrounding Gas on the Electroexplosive Tungsten Nanopowders Characteristics

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Abstract Tungsten nanopowders were produced by the method of wires electrical explosion in the different gases. The study of phase and dispersed composition of the powders was carried out. The influence of electrical parameters such as the value of energy input in wire and the arc stage of the explosion was discussed. The factors that make for decreasing the particles size are the lower pressure of surrounding gas and the use of addition of chemically reactive gas.

Keywords: Electrical explosion of wires, Tungsten nanopowder, Particles size

1. Introduction

Tungsten is widely used for many defense and high temperature applications. It has the highest melting point of all metals (3422°C), low vapor pressure, good erosion resistance, low thermal expansion and the highest tensile strength [1]. Tungsten and its alloys are used for filaments in high power lamps and electronic tubes, for making heating elements, rocket engine nozzles, superalloys and catalysts [2-4]. Superalloys containing tungsten are used in turbine blades and wear-resistant parts and coatings. Nanosized powders of tungsten possess more attractive properties in comparison with this material having large grains [5-9], and therefore, the methods of tungsten nanopowders synthesis have been attracted wide attention.

In recent years the nanosized tungsten powders have been prepared using various methods, such as salt assisted combustion reaction [10], chemical vapor synthesis [11], high energy ball-milling [12], physical vapor deposition [13], etc. However, these methods involve multi-steps and have the relatively low production rate, high energy consumption.

The process of wires electrical explosion (WEE) is widely used for production of metallic nanopowders and chemical compounds nanopowders [14, 15]. The WEE is a nonequilibrium process in which a wire under the effect of a pulse current becomes dispersed and mixed with the working ambient in the discharge chamber. The technology for producing nanopowders based on the phenomenon of WEE has been extensively developed in the world [16-20].

In pulsed fast processes like WEE the formation of nanoparticles happens in strongly nonequilibrium conditions with stabilization of metastable states in them that gives higher activity to nanopowders in many processes.

The method of WEE has a lot of advantages in comparison to others methods [14]. An important advantage of WEE-technology is the possibility of control over properties of WEE products including particles size, phase and chemical composition of nanopowders by means of electrical parameters. The WEE-technology, unlike other technologies, allows using the same installation to produce nanopowders of metals, alloys, intermetallic compounds, and chemical compounds depending on working gas in discharge chamber.

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High melting temperature of some metals such as tungsten and a considerable difference between metals melting and boiling temperature is not an obstacle of WEE method. The wire of such metal as tungsten can be easily dispersed through electrical explosion.

Nanosized tungsten has been prepared by the method of WEE and its phase composition and surface properties have been studied [21]. It was stated that phase composition of electroexplosive tungsten powders includes polymorphic modifications α-W and β-W, and the surface layer of tungsten particles forming at passivation in air, consists of oxide W_3O. The peculiarity of tungsten powder, which was produced by the WEE method, is formation of β-W phase. This phase has a lower X-ray density (19.1 g/cm^3) in comparison with α-W (19.3 g/cm^3). The oxide layer of the finest fraction of powder is well-crystallized oxide W_3O [21]. The largest particles are covered with amorphous oxide layer, element composition of which is closed to WO_2. Content of β-W in electroexplosive tungsten powder amounts to 30…40 wt%. The increase of the specific energy input in the wire results in the rise of contents β-W. This fact is explained with the increase of the velocity of the WEE products expansion, and, consequently, with the increase of velocity of cooling the scattering products of explosion. It brings to stabilization of high-temperature modification β-W. At the same time, in [21] there is not information about the influence of the composition of surrounding gas in the discharge chamber and the value of arc stage energy on characteristics of tungsten powder.

It is well known that the dispersiveness and other characteristics of nanopowders formed at WEE is a function of preparation conditions [14, 15, 22, 23]. In our present work, we report the effect of the WEE energy parameters such as energy input in the wire and energy of the arc stage, the working gas composition in the discharge chamber for the particles size, produced by electric explosion of tungsten wires.

2. Experimental Details

The principal scheme of the industrial installation UDP-4G for producing the powders by WEE method is shown in Fig. 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 the wire 4 in the electrodes gap between the high-voltage 5 and ground 6 electrodes. When the wire reaches the high-voltage electrode 5, the commutator 7 operates, and the electric discharge of the capacitor battery occurs on this part of the wire, after that the wire explodes. Obtained powder collects in the powder collector 8. Gas refined from powder is given back in the discharge chamber 10 by means of the ventilator 9. The discharge chamber 10 is vacuumed before working, and then the chamber is filled with working gas by means of system 11.

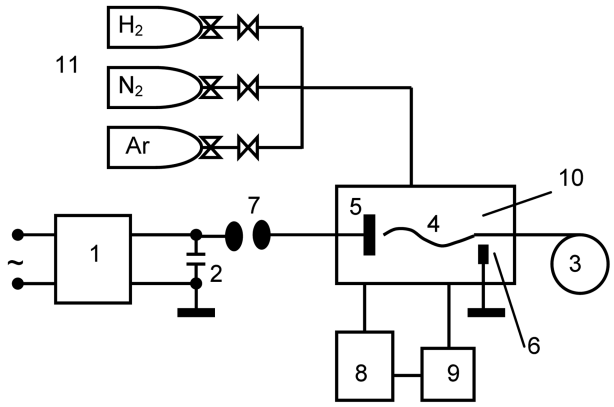


Fig. 1. Principle scheme of experimental installation: 1- high-voltage power source, 2-capacitor battery, 3-wire driving mechanism, 4-exploding wire, 5-high-voltage electrode, 6-ground electrode, 7-commutator, 8-powder collector, 9-ventilator, 10-discharge chamber, 11-system of filling with working gas.

As working gas for production of tungsten powder the following gases were used: 1) the gases at the pressure P of $1.5 \cdot 10^5$ Pa: argon (Ar); Ar with addition of 10 vol.% nitrogen (N_2); pure N_2; N_2 with addition of 5 vol.% hydrogen (H_2); 2) N_2 at the pressure of $0.3 \cdot 10^5$ Pa. The metal powder produced in inert gases self-ignites immediately after the contact with 100%-air. Thus, the passivation procedure is required with low oxidation by following medium: working gas +0.1 vol.% air [21].

The tungsten wires with diameter $d = 0.2…0.3$ mm and length $l = 50…80$ mm were used in the experiments. Electrical explosion of wires was carried out under conditions of "fast" explosion with an arc stage. 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 1.5e_s (e_s is the sublimation energy of the wire

material); the energy of the arc stage $(e_a) - (0.7\ldots1.7)e_s$. Parameters of electric circuit: capacitance $C = 2.25$ μF; charging voltage $U = 15\ldots30$ kV; inductivity $L = 0.58$ μH.

The phase analysis of the obtained powder was performed using CuK_α-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 (SEM). The determination of specific surface area (S_{sp}) was carried out by using a method of low temperature nitrogen adsorption (BET). The particle size distributions of obtained powders were measured using the analyzer "Mastersizer 2000". The differential-thermal analysis (DTA) and thermogravimetric analysis (TGA) was performed with apparatus Q-1500.

3. Results and Discussion

3.1. The influence of energy parameters of WEE on the dispersiveness

To investigate the influence of energy parameters of WEE on the dispersiveness of the tungsten powders argon at the pressure $1.5 \cdot 10^5$ Pa was used as working ambient in discharge chamber. The diameter of the wires in these experiments was 0.2 mm. The experimental conditions of the powder production and the results of the powders characterization are shown in the Table 1. The BET equivalent spherical particle diameter a_s was calculated for powders as $a_s = 6/(\rho_p S_{sp})$, where ρ_p is the density of tungsten After this paragraph in 3.1 the following text (see as Fig. 2).

Fig. 2 shows the dependences of the specific surface area of the electroexplosive tungsten powders on the specific electrical energy input in the wire (a) and the specific electrical energy of the arc stage (b). The increase both of the energy input in the wire and of the energy of the arc stage causes the rise of the specific surface area.

Table 1. Characteristics of electroexplosive tungsten powders depending on energy parameters

No	U, [kV]	l, [mm]	e/e_s	e_a/e_s	S_{sp}, [m^2/g]	a_s, [nm]
1	28	80	0.87	0.76	1.9	164
2	28	60	0.81	1.26	1.8	173
3	28	50	0.64	1.67	1.9	164
4	23	50	0.68	0.98	1.7	183
5	20	50	0.48	0.73	1.6	195

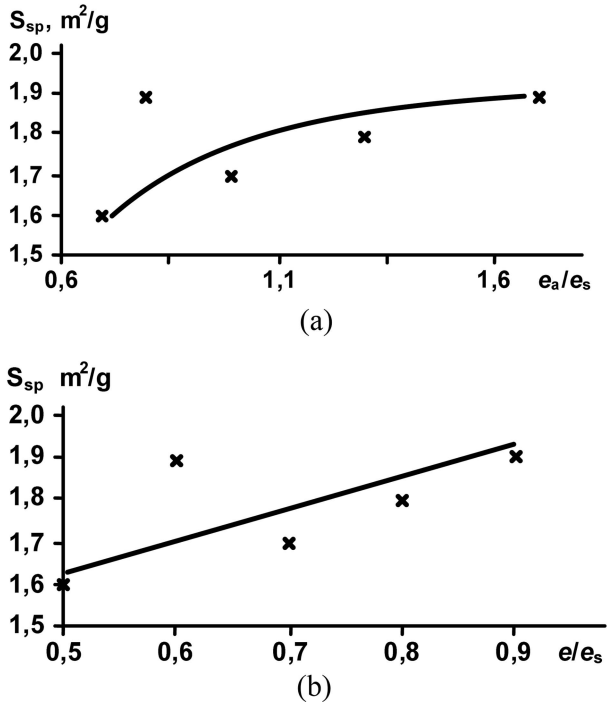


Fig. 2. Dependences of specific surface area of electroexplosive tungsten powders on the specific electric energy input in the wire (a); the specific electric energy of the arc stage (b).

Table 2. Characteristics of electroexplosive tungsten powders depending on working gas composition in the discharge chamber

No	Gas	S_{sp}, [m^2/g]	a_s, [nm]
1	Ar	1.5	207
2	Ar+10 vol% N_2	1.8	173
3	N_2	1.9	164
4	N_2+5 vol% H_2	1.9	164

It is known that the increase of the energy input in the wire leads to the particles size decreasing in powder produced by WEE [14, 15]. The arc stage of electric discharge provides additional dispersing effect on the primary products of wires explosion as shown in Table 1.

3.2. The influence of working gas composition on the dispersiveness

The conditions of experiments and the results of the tungsten powders characterization, which were produced under the explosion in different gases, are presented in Table 2. In these experiments the diameter of the exploding wires $d = 0.2$ mm, the length $l = 60$ mm. Electrical explosion of wires was carried out under the following

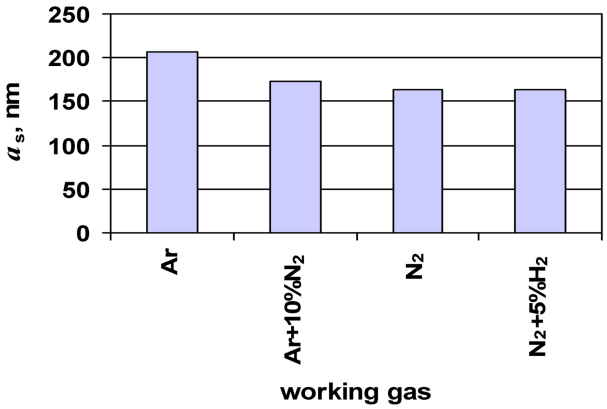


Fig. 3. Dependence of the BET-diameter of electroexplosive tungsten powders on composition of the working gas in the discharge chamber.

conditions: $U = 14$ kV; $e/e_s = 0.5$; $e_a/e_s = 0.7$. The gas pressure was $1.5 \cdot 10^5$ Pa.

Fig. 3 represents the average diameter values of obtained powders. According to these results, the composition of working gas in the discharge chamber influences greatly on the tungsten particles size. The powder with large specific surface area (1.9 m^2/g) and the smallest as (164 nm) was produced under the use of pure N_2 as surrounding ambient and under the addition of 5 vol.% H_2 in N_2 (the samples 3 and 4, Table 2).

We suppose that formation of chemical compound W_2N happens on the metallic particles surface. The protective layer of the chemical compound prevents from particle coalescence and reduces their size. At the same time, in accordance with the X-ray data the particles of the tungsten powder contain only metallic tungsten coated with a layer of oxide due to the process of the passivation and oxidation by air [21].

3.3. The influence of gas pressure on the dispersiveness

Nitrogen at the pressure $1.5 \cdot 10^5$ Pa and $0.3 \cdot 10^5$ Pa was used as working gas in the discharge chamber in the experiments for investigation of the gas pressure influence on the dispersiveness of the tungsten powders. The diameter of the wires in these experiments was 0.3 mm. The length of the exploding wires was 60 mm. Electrical explosion of wires was carried out under the following conditions: $e/e_s = 0.7$; $e_a/e_s = 0.8$ at the gas pressure $P = 1.5 \cdot 10^5$ Pa; $e/e_s = 0.4$; $e_a/e_s = 0.9$ at $P = 0.3 \cdot 10^5$ Pa.

Table 3. Characteristics of electroexplosive tungsten powders depending on the gas pressure in the discharge chamber

No	P, [10^5 Pa]	S_{sp}, [m^2/g]	a_s, [nm]
1	1.5	1.7	183
2	0.3	2.6	120

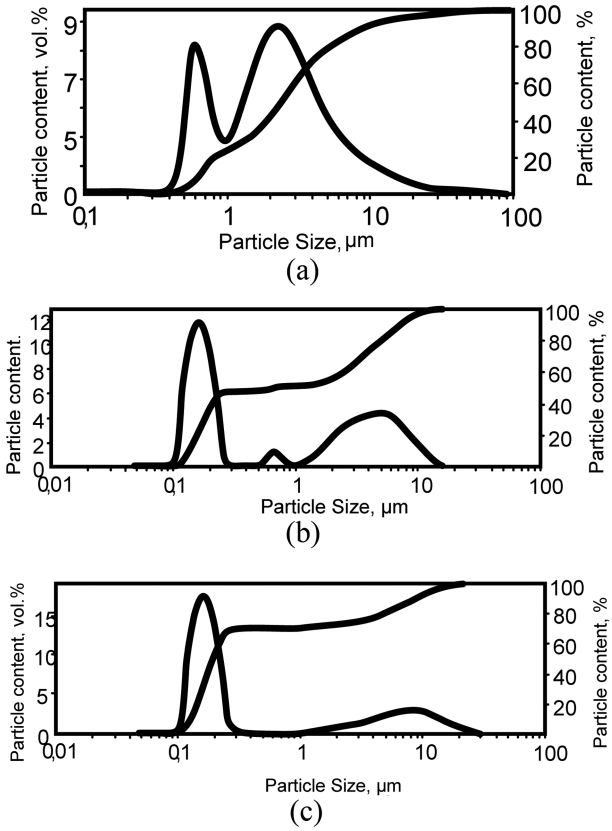
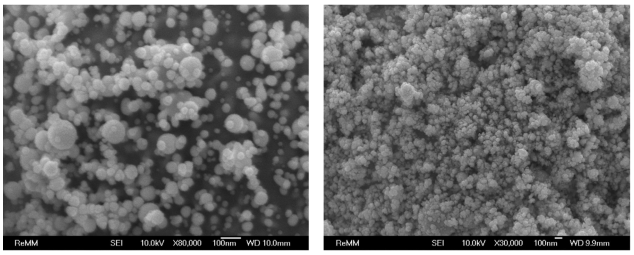


Fig. 4. Particle size distribution of the tungsten powder produced in Ar, P=1.5·10^5 Pa (a), in N_2, P=1.5·10^5 Pa (b), in N_2, P=0.3·10^5 Pa (c).

Characteristics of tungsten powders depending on the gas pressure in discharge chamber are presented in Table 3.

The tungsten powder with the largest surface area (2.6 m^2/g) was produced under the use of N_2 at the pressure $0.3 \cdot 10^5$ Pa. In case of the lower pressure in the explosive chamber the density of WEE-products in process of expansion reduces quicker than under the explosion in conditions of higher pressure, and the probability of coagulation and sintering particles decreases.

According to the particle size analysis, the obtained tungsten powders have as a rule three-modal size distribution (Fig. 4). If kind of working gas changes from Ar on N_2 at the pressure $1.5 \cdot 10^5$ Pa in the discharge chamber, the diameter of the produced particles corresponding to the first maximum on the size distribution curve



(a) (b)

Fig. 5. SEM images of tungsten powder, produced in mixture N_2 and Ar at P = 1.5·10^5 Pa (a), in N_2 at P = 0.3·10^5 Pa (b).

decreases from 0.686 to 0.169 μm, and the average diameter decreases from 2.404 to 0.694 μm (Fig. 4a and b). If N_2 was used as the working gas at the different pressure, the diameter of the particles corresponding to the first maximum does not change and it is 0.169 μm. However, the average diameter decreases from 0.694 to 0.196 μm, when the nitrogen pressure was reduced from 1.5·10^5 to 0.3·10^5 Pa (Fig. 4b and c). The first maximum of the particles in the size distribution curve increases correspondingly. Besides, the study of the particle size distribution demonstrated us that number of particles related to the first maximum increases with increasing the energy rate.

It is to be noted that there are no the nanosized particles in the size distribution curves. Obviously this fact can be linked to the agglomeration in the powders. The agglomeration can influence the particle size distribution measured by laser scattering. However, according to the electronic microscopy investigation there is the fraction of particles in powder, diameters of which are less than 100 nm (Fig. 5). The particles of the tungsten powder have spherical shape and smooth surface. It is noticeable that all particles present spheres that point to passing them through liquid state and on the action of the surface tension forces.

The activity of the prepared tungsten powders was estimated by the method of DTA-DTG under linear heating (15ºC/min) in air with the following parameters: the temperature at which the first stage of oxidation started (T_1, ºC) and the second stage of oxidation started (T_2, ºC), the degree of transformation (the oxidation level) of powders at temperatures ≤1000°C (α, %), and the maximum oxidation rate (v_{ox}, %/s). These parameters are presented in Table 4. Typical DTA-DTG curves of electroexplosive tungsten powder are shown in Fig. 6.

Table 4. Thermal stability of powders prepared by electroexplosions of tungsten wires under the heating in air

No (from Table 2)	T_1, [°C]	T_2, [°C]	α, [%]	v_{ox}, [%/s]
1	310	465	23.7	0.006
3	310	470	23.8	0.007
4	320	475	23.9	0.007
9	310	515	23.7	0.009

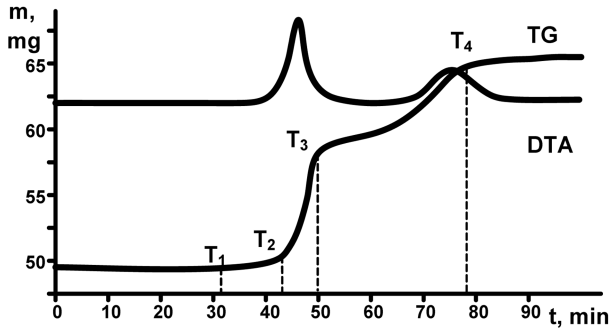


Fig. 6. Typical DTA-DTG curves of tungsten nanopowder: TG-temperature dependence of powder weight loss; DTA-temperature dependence of heat release at the heating.

The process of oxidation has three stages. The second stage is the stage of intensive oxidation. In the examined samples the temperature at which the second stage of oxidation started (T_2) depends on the surroundings and the gas pressure considerably: T_2 increases if the addition of chemically active gas were used and at the lower pressure. The powder obtained by electrical explosion in N_2 at the pressure 0.3·10^5 Pa has the maximum oxidation rate v_{ox}. This fact is explained with the greatest dispersiveness of this powder.

Thus, the parameters of thermal stability of the powders prepared by tungsten wire electroexplosions are closely correlated with their dispersiveness.

4. Conclusion

The size of tungsten particles produced by the electrical explosion of wires is defined with the specific electrical energy input in the wire and energy of the arc stage. The specific surface area of electroexplosive tungsten powders depends on the composition of the working gas in the explosive chamber. The use of chemically reactive gas N_2 as working ambient permitted to increase the value of the specific surface area of the powder due to formation of chemical compound protective layers on the metallic particles surface. The most significant parame-

ter of the particles size regulation is the use of low pressure of working gas in the discharge chamber ($0.3 \cdot 10^5$ Pa and lower).

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