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Production and characterization of molybdenum nanopowders obtained by electrical explosion of wires

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The characteristics of nanopowders obtained by the method of electrical explosion of molybdenum wires were investigated: the particle diameters, the particle size distributions. Controlling factors were electrical parameters and composition of surrounding gases in the explosive chamber. The molybdenum powders having maximum dispersiveness were produced using nitrogen as surroundings during explosion. The thermal activity of the prepared molybdenum powders at the heating in air has been studied.

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Keywords: Electrical explosion of wires, Molybdenum nanopowders, Dispersiveness

1. Introduction

Molybdenum metal is widely used in electrical and electronic devices, material processing, high temperature furnaces and equipment because of its high strength up to 2000 °C, low coefficient of expansion combined with good thermal and electrical conductivity, high resistance to corrosion by molten glass, salts and metals, and good resistance to abrasion and wear in thin coatings [1, 2].

Preparation methods of metallic molybdenum include vaporstate reduction of $MoCl_5$ with hydrogen, hydrogen reduction of molybdenum oxide, thermo-decomposition of carbonyl molybdenum, and plasma reduction. However, it is difficult to produce nanosized molybdenum using the methods listed above [3]. Nanosized powders of molybdenum possess more attractive properties in comparison with this material having large grains, and therefore, its synthesis has been attracting much attention.

Electrical explosion of wires (EEW) is widely used for production of metallic nanopowders and chemical compounds nanopowders [4, 5]. Applicability of EEW-method for production of such refractory metal as tungsten is shown in [5, 6]. The dispersiveness of electroexplosive powders depends on energy characteristics of explosion – value of the energy input into a wire before explosion and the arc stage energy of discharge.

In the present study the method of electrical explosion of wires was applied for preparation of molybdenum nanopowders. The effect of the arc stage energy and the working gas composition on the dispersiveness of powders was investigated.

2. Experimental details

The principal scheme of the industrial installation UDP-4G for producing electroexplosive powders is shown in the 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 wire length 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 part of the wire and as a result 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.

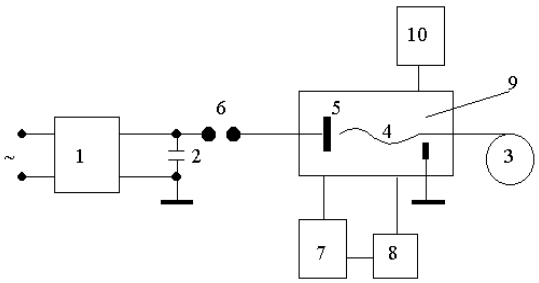


Fig. 1. Principle scheme of installation UDP-4: 1 - high-voltage power source, 2 - capacitor battery, 3 - wire driving mechanism, 4 - exploding wire, 5 - high-voltage electrode, 6 – commutator, 7 - powder collector, 8 – ventilator, 9 – chamber, 10 – system of filling with working gas.

As working gas for production of molybdenum powders the gases were used: 1) argon (Ar), 2) Ar with addition 10 vol. % of nitrogen (N_2), 3) pure N_2, 4) N_2 with addition 5 vol. % of hydrogen (H_2). The pressure P of gases was $1.5 \cdot 10^5$ 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 [5].

The molybdenum wires with diameter d = 0.2 and 0.3 mm and length l = 60 and 70 mm. were used in the experiments. The impurity content in molybdenum wire was ~0.4 mass. %. 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) possessed the values $(0.8…1.0)e_s$ (e_s – the energy of sublimation of metal), the energy of the arc stage (e_a) – $(0.2…1.6)e_s$. Parameters of electric circuit: capacitance C = 2.32 μF; charging voltage U = 19…29 kV; inductivity L = 0.58 μH.

Morphology of the particles was observed by an electron microscope "JSM-840". The determination of specific surface area (S_{sp}) was carried out by a method of 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-1000.

3. Results and discussion

It is well known, that the increase of the energy input in the wire leads to the increasing the dispersiveness of electroexplosive powder [4, 6]. To investigate the influence of EEW-energy on the dispersiveness of the molybdenum powders the gas argon was used as working atmosphere. The wire diameter was 0.3 mm, the wire length was 70 mm. The conditions of the powder production and the measured values of specific surface area S_{sp} are shown in Table 1.

Table 1. Specific surface area of molybdenum powders depending on electrical parameters.

№	e/e_s	U, kV	e_a/e_s	S_{sp}, m^2/g
1	0.8	29	1.6	3.30
2	0.9	19	0.2	2.50
3	0.9	24	0.8	2.55
4	1.0	21	0.4	2.37
5	1.0	27	1.1	3.15

Change of charging voltage in these experiments from 19 to 29 kV had an influence on the value of the arc stage energy: e_a/e_s = 0.2…1.6. At the same time the value of the energy input into wire e/e_s changes slightly from 0.8 to 1.0. Therefore, it was impossible to determine the dependence of the powders dispersiveness on the energy input into wire in investigated range of energy values. The dependences of the specific surface area of the electroexplosive molybdenum powders on the specific electric energy of the arc stage e_a/e_s are shown in Fig. 2. The arc stage energy rise more than $1.0e_s$ causes the increase in dispersiveness.

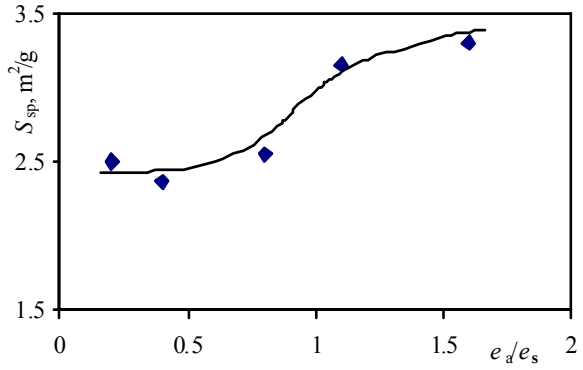


Fig. 2. Dependence of the specific surface area of molybdenum powders on arc stage energy.

According to the particle size analysis, the obtained molybdenum powders have three-modal size distribution (Fig. 3) that is typical for all electroexplosive nanopowders. It is determined by mechanism of wire destruction [4, 6]. The first maximum is corresponding to the particle diameters of 110…120 nm, the second maximum – 600…900 nm, the third maximum – 3000…8000 nm.

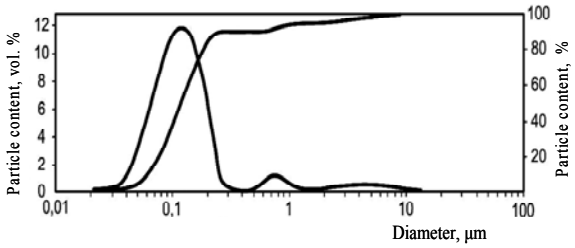
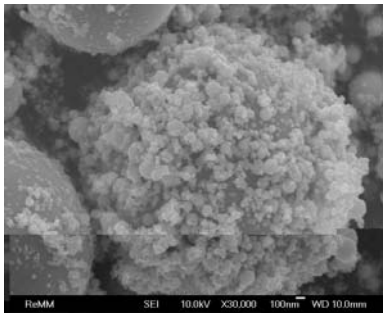


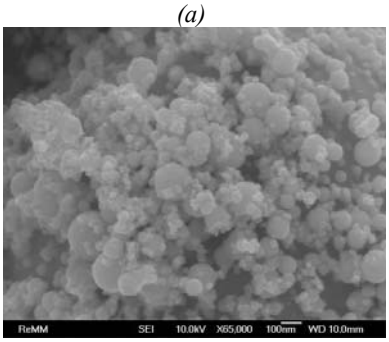
Fig. 3. Particle size distribution of the molybdenum powder (Sample 3, Table 1).

According to the electronic microscopy study, the particles of the molybdenum powder have spherical shape and unsmooth surface (Fig. 4). Along with particles of micrometer fraction there is the fraction of particles in powder, diameters of which are less than 100 nm. The fine particles cover the surface of the large particles and form the individual agglomerates. 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.

To investigate the effect of the working gas composition in the explosive chamber on the dispersiveness the following gaseous mixtures were used: 1) Ar, 2) Ar + 10 vol.% N_2, 3) N_2, 4) N_2 + 5 vol.% H_2. The experiments conditions and the values of specific surface area of the molybdenum powders, which were obtained under the explosion in different gases, are presented in Table 2. The diameter of the exploding wires in these experiments was 0.2 mm, the length was 60 mm.



(a)



(b)

Fig. 4. Microphotos of the electroexplosive molybdenum powder (Sample 3, Table 1).

Table 2. Specific surface area of molybdenum powders depending on working gas composition.

№	U, kV	e/e_s	e_a/e_s	Gas	S_{sp}, m^2/g
1	12.4	0.6	0.6	Ar	3.4
2	12.4	0.7	0.5	Ar+10 vol.% N_2	3.5
3	12.4	0.7	0.5	N_2	4.9
4	12.4	0.7	0.5	N_2+5 vol.% H_2	2.4
5	15.1	0.8	1.1	Ar	3.5
6	15.1	0.8	1.1	Ar+10 vol.% N_2	3.1
7	15.1	0.9	1.0	N_2	3.6
8	15.1	0.9	1.0	N_2+5 vol.% H_2	2.9

The dependence of the specific surface area of molybdenum powders obtained in various gases is shown in Fig. 5. The molybdenum powders having maximum dispersiveness in conditions of this experiment (S_{sp} = 4.9 m^2/g) were produced using nitrogen as surrounding ambient during explosion. This result can be explained by formation of the thin films of chemical compound Mo_2N on the molybdenum particles surface, that prevents from coalescence and increase in size.

Thus, the use of nitrogen as working gas in the explosive chamber permitted to increase the value of the specific surface area to 4.9 m^2/g in comparison with use of argon (S_{sp} = 3.4 m^2/g).

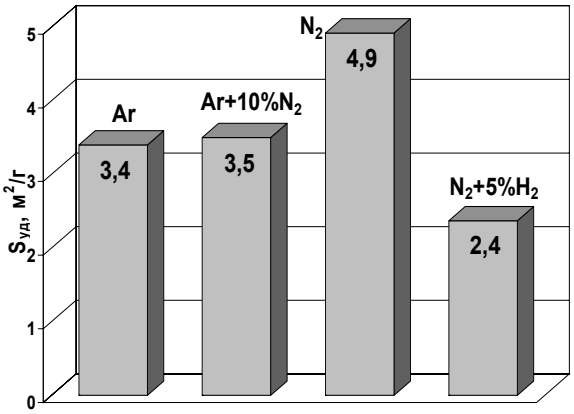


Fig. 5. Dependence of the specific surface area of molybdenum powders on working gas composition (U = 12.4 kV).

The activity of the prepared molybdenum powders was estimated by the method of DTA-DTG under linear heating (15 ºC/min) in air with the following parameters: the temperature at which the first stage of oxidation started (T_1, °C) and the second stage of oxidation started (T_2, °C), the degree of transformation (the oxidation level) of powders at temperatures ≤1000°C (α, %), and the maximum oxidation rate (v_{ox}, %/s). The oxidation process of powder obtained in argon at e/e_s = 0.6 and e_a/e_s = 0.6 is characterized with a mass increasing of the sample and has two stages with maximum 441 ºC and 517 ºC (Fig. 6). The first stage is connected with oxidation of small-sized particles, the second stage – with large-sized particles. The temperature of the oxidation beginning T_1 = 350 ºC and T_2 = 452 °C. At the further heating (784 ºC) a drastic mass decrease is observed, related to molybdenum (VI) sublimation. According to the thermal analysis results the degree of transformation α = 42.3 %; the maximum oxidation rate V_{max} = 0.007 %/s, the specific heat effect is 3299 J/g.

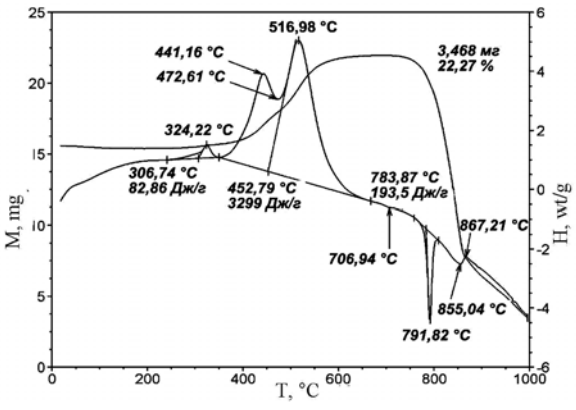


Fig. 6. Thermogram of molybdenum powder (Sample 1, Table 2).

4. Conclusions

The nanosized molybdenum powders were produced by electric explosion of wires in argon, in nitrogen and in gases mixtures. As it can be seen from the experimental data, the dispersiveness of the molybdenum powders depends on the value of the arc stage energy, which defined with the ratio of the length and diameter of wires, and the value of charging voltage. The most significant parameter of the dispersiveness regulation is the use of reactive gas as working atmosphere in the explosive chamber, for example, nitrogen. The increase of the specific surface area is explained with formation of protective thin films (Mo_2N) on the particles surface during the process of electrical explosion of wires.

References

[1] E. R. Braithwaite, J. Haber, Molybdenum: An Outline of its Chemistry and Uses, Elsevier, New York, 1994.
[2] P. Garg, S. J. Park, R. M. German, Int. J. of Refractory Metals & Hard Materials **25**, 16 (2007).
[3] Y. Lia, G. Luoa, Y. Fan, Y. Chen, Materials Research Bulletin **39**, 195 (2004).
[4] Y. S. Kwon, A. P. Ilyin, D. V. Tikhonov, O. B. Nazarenko, G. V. Yablunovskii, in Proc. of the 7th Korea-Russia International Symposium on Science and Technology KORUS'2003, Ulsan, **1**, 175 (2003).
[5] Y. S. Kwon, A. A. Gromov, A. P. Ilyin, A. A. Ditts, J. S. Kim, S. H. Park, M. H. Hong, Refractory Metals & Hard Materials **22**, 235 (2004).
[6] A. P. Ilyin, O. B. Nazarenko, D. V. Tikhonov, J. Optoelectron. Adv. Mater. **10**(3), 645 (2008).

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