RESEARCH INTO NANOPARTICLES OBTAINED BY ELECTRIC EXPLOSION OF CONDUCTIVE MATERIALS

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Introduction

To satisfy the growing demand for nanoparticles in the world market, manufacturers are increasing an extent of their production while researchers are developing modern methods of nanoparticles production or updating the existing ones. Among a number of their production methods there are Catalytic Chemical Vapor Deposition [1], Explosion [2], Electro-Explosion [3, 4], Laser Induced Chemical Vapor Deposition [5], Mechanical Milling [6], Sol-Gel [7], Plasma Physical Vapor Deposition [8]; Wet Chemistry [9] and the others.

Theoretical analysis

One of the primary nanoparticles production methods is electric explosion of wire (further – EEW) which is known as a physical phenomenon since 1771. EEW is the nanoparticles production technology of "electric explosion of conductive materials" when high-voltage (15–30 kV) and powerful (density 10^{11}–10^{12} A/m^2) impulse (duration 10^{-4} –10^{-7} s) flows through a conductor (wire). In EEW low electric densities - E/E_S 0,8–1,5 (where E – comparative explosion energy, E_S – sublimation energy of exploded material) are used [10].

Limitation of EEW as a method of nanoparticles production lies in a great dispersion of particle diameters – a spectrum of nano- and micrometric diameters (10^3 and higher differences in diameters are likely). When using the wire of a relatively wide diameter (0,43 mm) a likely particles diameter is 1–3 μm [10]. Wire of 0,25–0,3 mm used for nanoparticles production restricts their productivity [11, 12]. In Argone (10^5 Pa) exploding copper wires of 0,43 mm diameter when reaching energy density E/E_S higher than 2,1 the average particles diameter becomes less than 100 nm [11]. Due to great differences in nanoparticles diameters formed by explosion (in aerosol conditioned by explosion), a continuous separation of nanoparticles from aerosol flows is essential.

Dispersion of conductor explosion products is mostly affected by a diameter of wire, density of comparative energy, duration of the energy input. The wire diameter being smaller, the greater energy density is introduced and the duration of energy separation is shorter, thus due to the higher internal pressures and temperature of the material the diameters of nanoparticles are smaller [13]. The studies of the basic EEW phenomena have been generalized by Russian scientists [14–16]. This process consists of (resistant) incandescence of hard metal up to its melting temperature, fusion, intensive heating of melted wire metal (under surface and internal evaporation), surface and internal evaporation, formation of material layers of different densities and the explosion which is accompanied by complicated hydrodynamic phenomena, such as a sudden material extension violating an electric conductivity mechanism, ionization – shunting output by wire vapour, formation and spread of the drops flow, cooling (under inert gases) [14–16]. EEW is simulated by a digital method, however the opinions differ as to the conductor explosion mechanism [17].

In contrast to formation of coatings by EEW, in production of nanoparticles the speed of particles is of no importance. For this reason an assumption may be made that the lower rates of the current input may be used (the current impulse penetration is deepened i.e.- the skin), while with an increase in the wire diameter the wire temperature and pressure are increased during the explosion, thus increasing dispersion of the products. The lower voltage (5 kV) ensures lower energy input rates (10–50 μs). Technical parameters of the up-to-date impulsive current sources (output frequency and power) significantly exceed the potential of an explosion technology device (explosions frequency is restricted by a spontaneous short-circuit risk), therefore the real potential for an increase in production efficiency is an increase in a wire diameter.

Objective of this research is to investigate the vista of producing nanoparticles by EEW at low voltage and high energy surplus using the wire of an enlarged diameter.

Research tasks involve: the production of iron and copper nanoparticles at 5 kV voltage with a great energy surplus using the wire of 0,3–0,5 mm diameter, the assessment of produced particles by SEM and XRD methods and the assessment of a newly developed separation system.

Research methodology

Copper and iron nanoparticles are produced by the EEW device whose characteristics are: voltage of batteries – up to 5 kV, volume – 0,2 mF, energy – up to 2500 J, frequency of output – 0,25 Hz.

To separate nanoparticles a separation device is used which consists of a settler and a three stages centrifugal cyclone and a fan (Fig. 1). The settler is intended for separating gravitational micrometric particles from aerosol.

Particles are produced in the air (pressure 10^5 Pa). Analyses have been made by exploding the iron wire of 60 mm length, 0,31 and 0,45 mm diameter and the copper wire of 0,38 and 0,49 mm diameter. Purity of the wire material is 99,5% of iron and 99,9% of copper.

To obtain the ultimate dispersion of particles and uniformity of diameters a high energy surplus is selected notwithstanding the fact that it increases the area of particles surfaces and their temperature i.e. their interaction with the environment. The comparative exploding energy (Cu wires of 0,06 and 0,1 g mass) has been analytically determined to be from 4 to 8 times greater than that of copper sublimation energy ($E_{S.Cu}$ – 5,4 kJ/g).

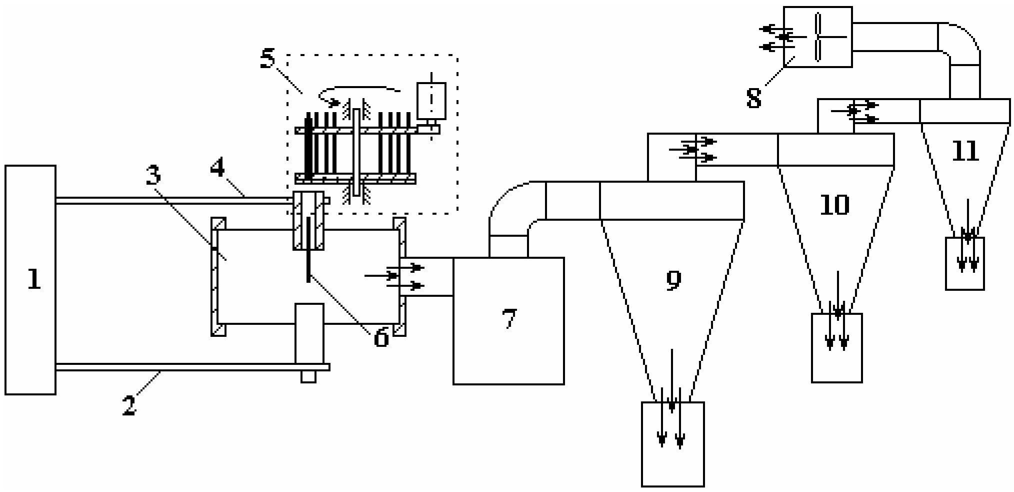


Fig. 1. Schematic diagram of nanoparticles production device: 1 – source of high voltage current pulses; 2 – bus of current input (+); 3 – injection chamber; 4 – bus of current input (-); 5 – supply mechanism of wire segments and a gear; 6 – exploded wire segment; 7 – settler; 8 – fan; 9 - cyclone of large particles; 10 – cyclone of medium particles; 11 – cyclone of small particles

Structural X-ray analysis of nanoparticles has been made according to the Breg-Brentan scheme by difractometer DRON 3.0 (Cu *K*α radiation), Ni-filter, 30 kV voltage, 30 mA current, turning the angle 2θ from 25 to 100°. X-ray photographs have been processed by XRLL Edit program.

Sizes and shapes of the particles have been analyzed by SEM JEOL-5600 enlarging them up to 500.000 times.

Effectiveness of nanoparticles production has been assessed by a material utilization coefficient (ratio of nanoparticles to the wire masses utilized for their production) with analytical scales KERN ABJ 120-4 m (accuracy – 0,1 mg).

Research results

EEW nanoparticles produced of iron and copper wire make heterogeneous, spongy and dark mass in which agglomerates are evident. The largest ones (of 2–10 μm diameter) are formed when exploding iron, Fig. 2. Agglomeration of copper particles is also perceptible whose size may be 1–7 μm (the smallest particles were collected in a smallest cyclone are of 1–3 μm, the largest ones – 5–7 μm were collected in a largest cyclone).

SEM analysis indicates that iron nanoparticles are of a regular sphere shape, whereas the shape of copper nanoparticles is not that of a sphere (Fig. 3) and their medium size is smaller than 100 nm. The sizes of separate large particles are 200–350 nm.

At different stages of a separation system the contamination of collected nanoparticles (20–80 nm) by individual large particles (250–400 nm) is conditioned by the unsteady air flow. Vapour formed during the conductor explosion (Fe > 2735, Cu > 2590 °C) is heating the air in the injection chamber, its pressure grows, so does the rate in settler and cyclones. With the variation in the air rate the separation parameters are also varying.

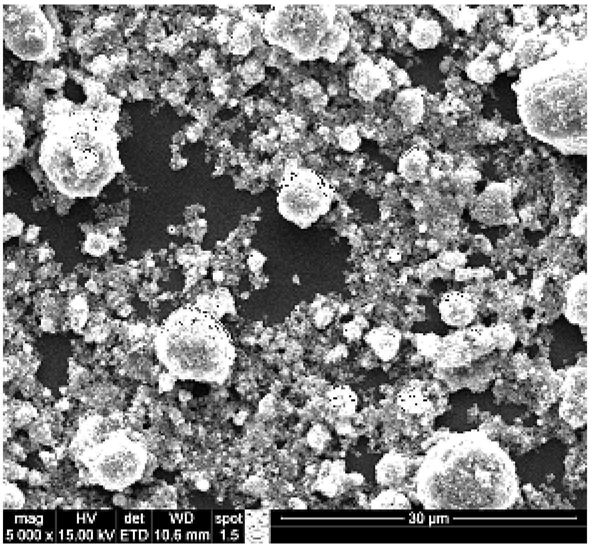


Fig. 2. SEM picture of iron nanoparticles (Ø0,31 mm wire) collected in a cyclone of large particles (×5.000)

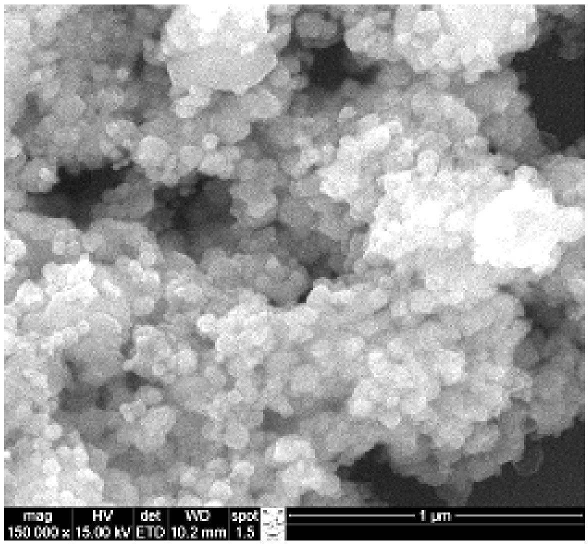
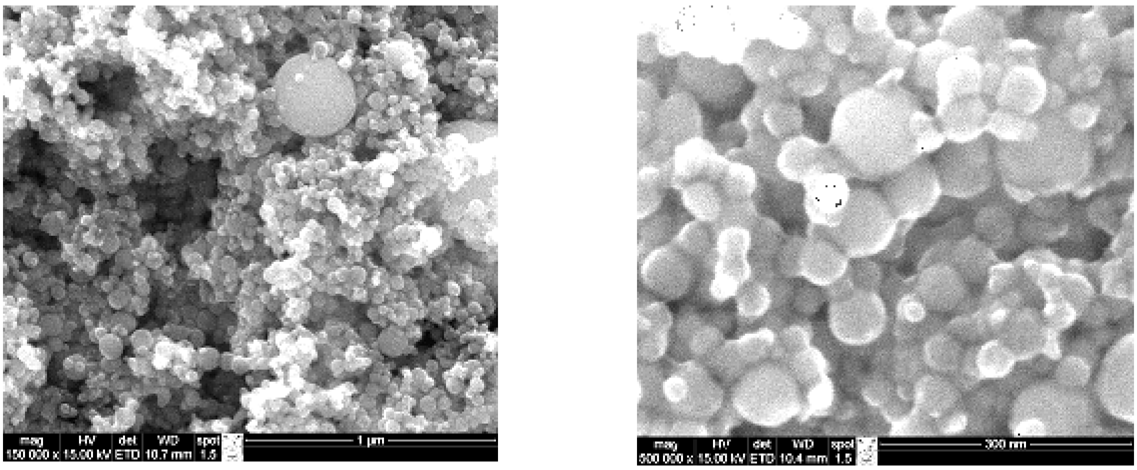


Fig. 3. SEM picture of copper nanoparticles (Ø0,38 mm wire) collected in a settler (×150.000)

Iron (Ø0,31 mm wire) particles of 50–80 nm collected in settler happen to be of 250–400 nm diameter, while micrometric particles are detected rather seldom. Among the particles of 30–60 nm (up to 100 nm) collected in the large particles cyclone the micrometric ones are detected, whereas in the medium particles cyclone they are 20–50 nm (up to 80 nm). SEM photos are presented in Figs 2–4.

A classical constructional solution of nanoparticles production device is a vertical aerosol flow movement (down) [11, 12]. Forming a horizontal aerosol flow (aerosol output gap being in the center of the chamber) the separation of nanoparticles begins even in the explosion chamber (micrometric particles remain there).

Histograms of diameters of Fe nanoparticles produced of 0,31 and 0,45 mm diameter wire collected in medium and large particles cyclones are presented in Fig. 5.



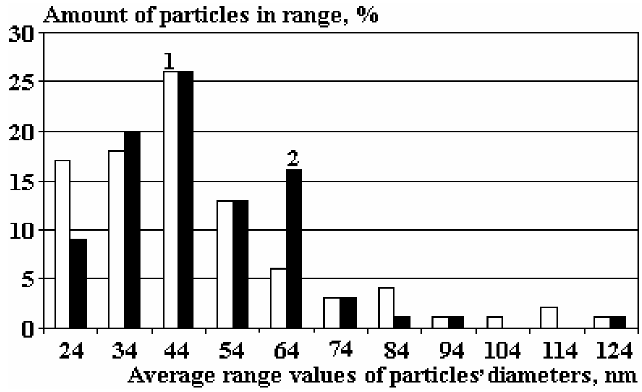
a *b*

Fig. 4. SEM photos (×150.000 and ×500.000) of iron nanoparticles (Ø0,31 mm wire) collected in the particles settler (a) and in the medium particles cyclone (b)

The particles whose average diameter is 46 nm are collected in the large particles cyclone of the exploded iron separation system, while those of 42 nm are collected in the medium particle cyclone.

As it has been expected when using the iron wire of larger diameter (0,45 mm) the produced nanoparticles are of larger than medium diameter – 69 nm. This size satisfies the requirements of many technologies. When nanoparticles are produced of Ø0,49 mm copper wire their average diameter is larger – 97 nm due to lower resistance and higher density of this metal.

To assess effectiveness of the cyclonic separation system the wires of iron (Ø0,31 mm) and copper (Ø0,38 mm) metal of masses 6 g and 11 g, respectively, have been exploded. Fig. 6 presents the collected particles masses in different separation stages (a) and their percentage distribution (b).



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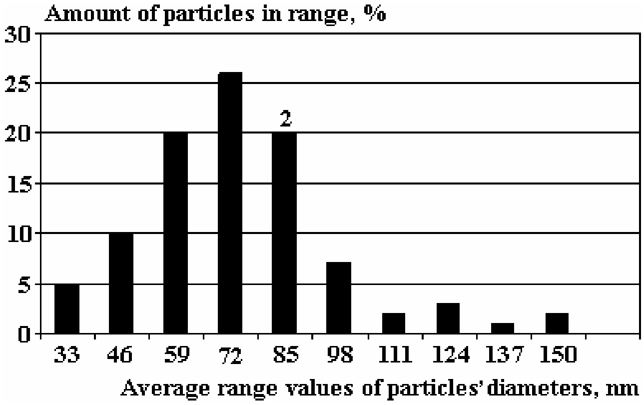
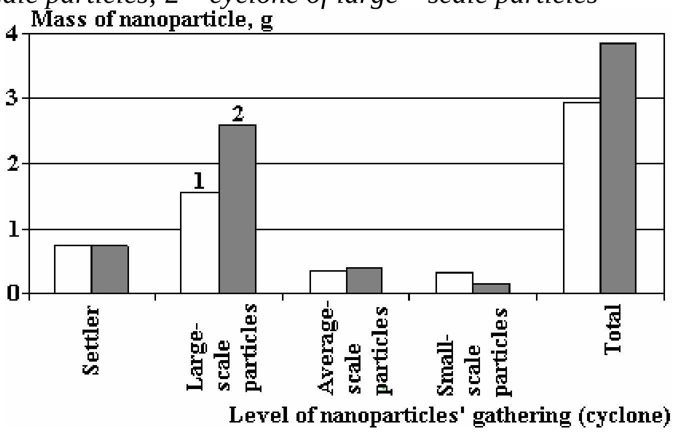


b

Fig. 5. Histograms of diameters of iron particles produced of 0,31 mm (a) and 0,45 mm (b) diameter wire. 1 – cyclone of average – scale particles; 2 – cyclone of large – scale particles



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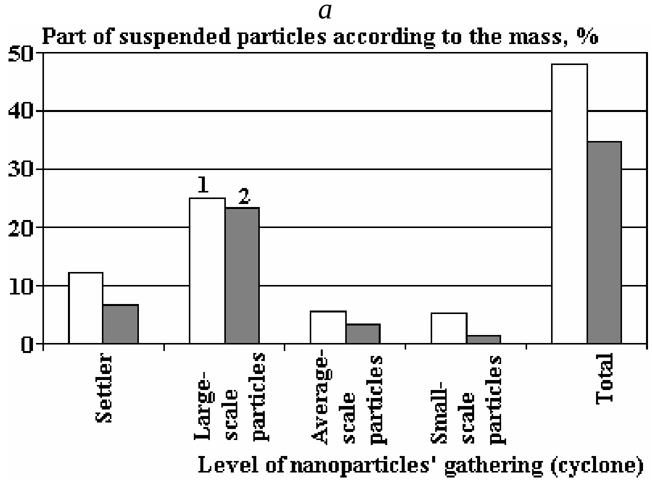
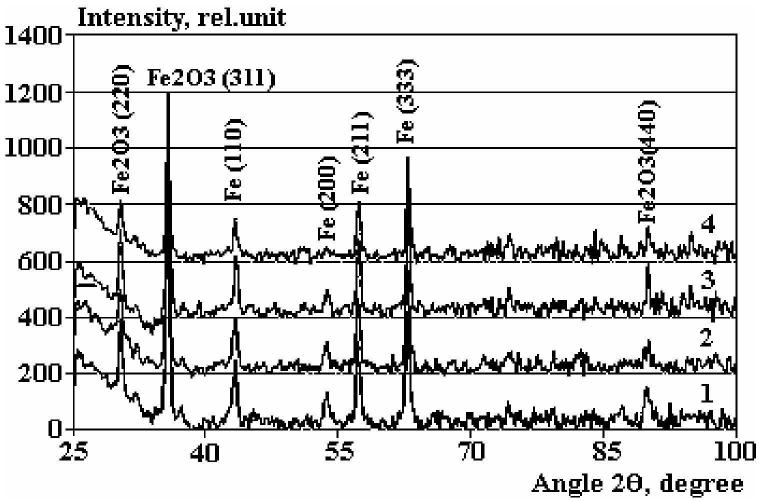


b

Fig. 6. Distribution of masses (a) and their percentage (b) of Cu and Fe nanoparticles collected at different separation device settler and cyclones. 1 – iron nanoparticle; 2 – copper nanoparticle

The material utilization coefficient in production of nanoparticles is determined 48% for iron and 35% for copper. According to the works by Suchara and other researchers during the EEW process about a half of exploded material evaporates [18]. The real material utilization coefficient is greater because it is impossible to collect nanoparticles from the surfaces of cyclones and settler fully.

XRD spectra of iron and copper nanoparticles collected in all stages of a separation device are given in Fig. 7. It should be noted that the spectra peaks indicate a negligible amount of pure iron and copper quantities. XRD spectra peaks of Cu nanoparticles in the interval of radiation incidence angle of 25–100 (2θ) degrees are quite identical. Here copper oxide (CuO) is prevailing. In the radiogram (Fig. 7,*b*) in the spectrum of pure copper there are two slight peaks (111 and 200). The analogous results are observable in the Fe radiogram (110 and 211) (Fig. 7,*a*). It is the result of the interaction of the air with nanoparticles during the production process.



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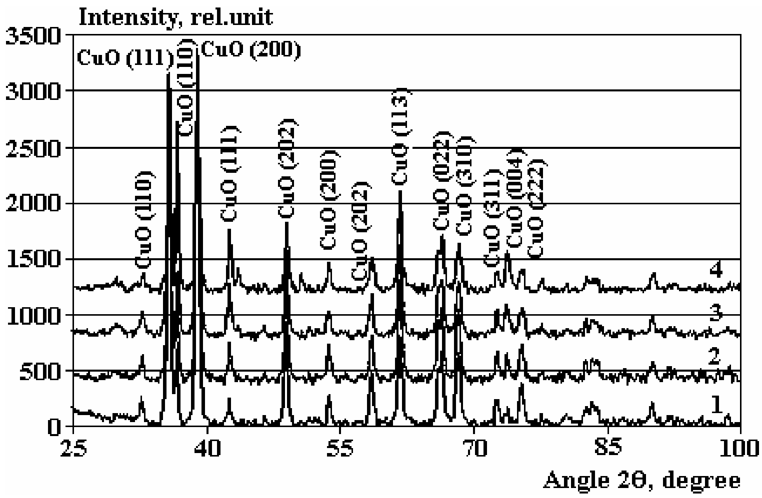

b

Fig. 7. XRD spectra of Fe (a) and Cu (b) nanoparticles collected in all separation stages (1 – in small particles cyclone, 2 – in medium particles cyclone, 3 – in large particles cyclone, 4 – in particles settler)

Discussion on results

In a settler the particles are separated on the principle of gravitation. Here about 10% of all particles are collected which have to be additionally sorted by airing them with a gas flow and repeatedly supplying them to the cyclones. According to the percentage amounts of iron and copper nanoparticles at the separation device stages the following conclusion can be drawn:

– iron particles are more effectively collected;

– collection of nanoparticles in a large particles cyclone is equivalent (23–25% of the utilized wire mass for production); Fe nanoparticles are on average collected twice more than Cu in a settler and small particles cyclones.

When comparing the diameter differences of the produced nanoparticles to those obtained by the other researchers [4, 29, 20], it should emphasized that the diameters of particles are more uniform.

Conclusions

1. An increase in efficiency of nanoparticles production can be achieved by applying low voltages, high energy densities and wires of enlarged diameters – 0,31–0,45 mm of iron (average nanoparticles diameter being 42–74 nm), and diameter 0,38–0,49 mm of copper (average nanoparticles diameter being 69–97 nm).

2. When producing nanoparticles the wire material utilization coefficients are high: Fe – 48%, Cu – 35%.

3. Electric explosion of a conductor in the air is relevant to production of oxides/metals – oxide nanoparticles (Fe and Cu oxides of different crystollagraphic axes are formed (Fe_3O_4, Fe_2O_3, CuO, Cu_2O) with a moderate quantity of pure Fe and Cu metals (Fe(110), Fe(211), Cu(111), Cu(200)).

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REFERENCES

1. Choi J.W., Sohn H.Y., Choi Y.J., Fang Zh.Z. Chemical vapor synthesis and characterization of aluminum nanopowder. *Journal of Power Sources.* 2010, **195**(5),1463–1471.
2. Vul' Alexander Ya. Characterization and Physical Properties of UNCD Particles. *Ultrananocrystalline Diamond*. 2006, 379–404.
3. Fu Y., Shearwood Ch. Characterization of nanocrystalline TiNi powder. *Scripta Materialia*. 2004, **50**(3), 319-323.
4. Kwon Y.S., Ilyin A.P., Tikhonov D.V., Yablunovsky G.V., An V.V. Characteristics of nanopowders produced by wire electrical explosion of tinned copper conductor in argon. *Materials Letters*. 2008, **62**, 3143–3145.
5. Morjana I., Voicua I., Dumitrachea F. et. al. Rand Carbon nanopowders from the continuous-wave CO laser- 2 induced pyrolysis of ethylene. *Carbon*. 2003, **41**, 2913–2921.
6. Wongmaneerung R., Yimnirun R., Ananta S. Effect of vibro-milling time on phase formation and particle size of lead titanate nanopowders. *Materials Letters.* 2006, **60**(12), 1447–1452**.**
7. Wang H., Zhang Q., Yang H., Sun H.. Synthesis and microwave dielectric properties of $CaSiO_3$ nanopowder by the sol–gel process. *Ceramics International*. 2008, **34**(6), 1405–1408.
8. Kouam J., Ait-Ahcene T., Plaiasu A.G., Abrudeanu M., Motoc A., Beche E., Monty C. Characterization and properties of ZnO based nanopowders prepared by solar physical vapor deposition (SPVD). *Solar Energy*. 2008, **82**(3), 226–238.
9. Carvalho J.F., De Vicente F.S., Pairis S., Odier P., Hernandes A.C., Ibanez A. Synthesis of YAP nanopowder by a soft chemistry route. *Journal of the European Ceramic Society*. 2009, **29**(12), 2511–2515.
10. Котов Ю.А., Яворский Н.А. Исследование частиц, образующихся при электрическом взрыве проводников. *Физика и химия обработки материалов*. 1978, (4), 24–29.
11. Лернер М.И. *Электровзрывные нанопорошки неорганических материалов: технология производства, характеристики, области применения*. Автореферат дисс. д.т.н. Томск, 2007. 31 с.
12. Назаренко О.Б. *Процессы получения нанодисперсных тугоплавких соединений и металлов методом электрического взрыва проводников*. Автореферат дисс. д.т.н. Томск, 2006. 22 с.
13. Kotov Yu.A. Electric Explosion of Wires as a Method for Preparation of Nanopowders. *Journal of Nanoparticle Research.* 2003, **5**, 539–550.
14. Иваненков Г.В., Пикуз С.А., Шелковенко Т.А. и др. *Обзор литературы по моделированию процессов ЭВ тонких металлических проволочек. Ч.1. Основные процессы ЭВП в вакууме*. М.: Физический институт им. П.Н.Лебедева РАН. 2004, 26 с.
15. Иваненков Г.В., Пикуз С.А., Шелковенко Т.А. и др. *Обзор литературы по моделированию процессов ЭВ тонких металлических проволочек. Ч.2. Физические свойства вещества с высокой плотностью энергии в разрядах через металлические проволочки*. М.: Физический институт им. П.Н.Лебедева РАН. 2004, 30 с.
16. Иваненков Г.В., Пикуз С.А., Шелковенко Т.А. и др. *Обзор литературы по моделированию процессов ЭВ тонких металлических проволочек. Ч.3. МГД модель развития разряда по завершении формирования системы плазменная корона – жидко-поровой керн*. М.: Физический институт им. П.Н.Лебедева РАН. 2004, 26 с.
17. Tkachenko S.I., Vorob'ev V.S., Malyshenko S.P. Parameters of wires during electric explosion. *Applied Physics Letters.* 2003, **82**(23), 4047–4049.

18. Сухара Т., Фукуда С., Ито Х. *Нанесение покрытий взрывающимися проволочками. Получение покрытий высокотемпературным распылением*. М.: Атомиздат, 1976. С. 124–133.
19. Sabari Giri V., Sarathi R., Chakravarthy S.R., Venkataseshaiah C. Studies on production and characterization of nano-Al_2O_3 powder using wire explosion technique. *Materials Letters*. 2004, **58**(6), 1047–1050.
20. Wang Q., Yang H., Shi J., Zou G. Preparation and characterization of nanocrystalline powders of Cu–Zn alloy by wire electrical explosion method. *Materials Science and Engineering A*. 2001, **307**(1–2), 190–194.

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Summary

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