

Electric explosion of wires as a method for preparation of nanopowders

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Received 15 March 2003; accepted in revised form 15 May 2003

Key words: burning, electrical explosion, metal wire, nanoparticles, nanopowders, oxides

Abstract

The development of the method of electric explosion of wires and research results concerning preparation of nanopowders by this method has been reviewed. The method is highly productive (up to 200 g/h), provides powders with an average particle size of 20–100 nm, and requires an energy consumption of about 25 kWh/kg. Several characteristics of the nanopowders will be given and their applications will be exemplified too.

Introduction

The phenomenon of electric explosion of wires (EEW) reduces to the following. When a high-density (10^4 – 10^6 A/mm²) current pulse, which is usually produced by the discharge of a capacitor bank, passes through a wire, the density of the energy in the wire may considerably exceed the binding energy because of a high rate of the energy injection and an expansion lag of the heated material. As a result, the material boils up in a burst, a bright light flashes, and a mixture of superheated vapor and boiling droplets of the exploding wire material and a shockwave scatter to the ambient atmosphere.

The character of the circuit current may vary considerably depending on parameters of the electric circuit (Figure 1a), such as capacitance C of the capacitor bank, inductance L of the discharge circuit, the charging voltage V_0 of the capacitors, characteristics of the exploding wire (material and geometrical dimensions), and parameters of the ambient atmosphere (density, electric strength, etc.). One may observe complete or part-time interruption of the current (Figure 1b), release of all the stored energy by the end of the explosion (Figure 1c), transformation of the current, which passes through the metal, to the plasma discharge current (Figure 1d), etc.

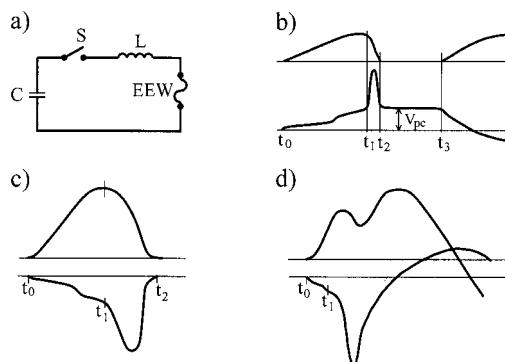


Figure 1. EEW circuit diagram (a) and current (top) and voltage oscillograms: current-pause explosion (b); V_{pe} – voltage left across the capacitor, t_0 – t_1 – heating of metal, t_1 – t_2 – explosion, t_2 – t_3 – current pause, $t > t_3$ – arc discharge; matched explosion (c); explosion with surface arc discharge (d).

Since EEW is simple to realize (a capacitor, a commutator, and connecting buses are needed only, Figure 1a), this phenomenon was first observed and described by Nairne as early as in 1774 (Chace, 1959). From that time on, it has been attracting attention of researchers for a number of possible applications.

EEW has been used successfully in environmentally insensitive fast exploding wire detonators (Leopold, 1964), since it provides the energy release density

sufficient for initiation of detonation. Such exploding wire detonators were used to cut bolts and control cables of rocket stages, as well as for initiation of charges used to loosen frozen soil or rocks before housing construction. Thanks to a good time reproducibility of initiation, this principle could be used for creation of preset-profile detonation waves, e.g. explosion current interrupters (Kotov & Tsipenko, 1984). Fast interruption of current was employed for creation of powerful opening switches and development on their basis of high-power compact generators and electron accelerators with an intermediate inductive energy storage (Kotov et al., 1976a,b). Complete interruption of current by EEW was used in high-voltage devices as quick-acting fuse (McFarlane, 1959). A bright flash was used for illumination during shadow photography of fast high-temperature processes (Vanyukov & Isaenko, 1962). EEW was used in many other applications too.

The EEW production of powders presents interest since a considerable overheat of the metal and the non-equilibrium process allow preparing powders with new properties and those, which are expensive or difficult to produce by other methods.

Apparently, the production of ultrafine powders by the exploding wire technique was begun by Abrams¹ (1946), who studied radioactive Al, U, and Pu aerosols. The process was found to yield sintered spherical particles, mainly 0.2 μm in size, which were connected into chains less than 1 μm long.

In Karioris and Fish (1962) it was found that this method is used in the generation of aerosols of 15 metals, namely Au, Ag, Al, Cu, Fe, W, Mo, Ni, Th, U, Pt, Mg, Pb, Sn, and Ta. The researchers showed the aerosol yield to depend on many conditions (the capacitor bank voltage and capacitance, the wire mass, and the character of the ambient gas). Particles 30–50 nm in diameter were obtained for every metal. It was shown that explosion of noble metals in air yielded metal particles, while explosion of a base metal generated a mixture of oxides and the metal. Explosion of a base metal in argon yielded metal particles. Also, the particle size distribution was constructed, but only for particles suspended in a gas. The researchers found that the particle size distribution was close to normal logarithmic, although bimodal distributions occurred too.

The possibility of producing Al and Mg iodides, sulfides, and carbides (Joncich & Reu, 1964), as well as Mg, Ti, Zr, Ta, Zn, and Al nitrides (Joncich et al., 1966)

was demonstrated. It was found, too, that exploding Fe, Pt, Cu, Cd, and Re did not give nitrides. Explosions were performed in the atmosphere of nitrogen, ammonia and hydrogen with nitrogen, and also in liquid nitrogen. The nitride yield was highest, up to 53%, when titanium was exploded. The yields were up to 56.5% for MgI_2 , 60.6% for MgS , 22% for AlI_2 , and 18.2% for Al_2O_3 . The carbide yield was very low.

Couchman¹ (1965) investigated particles produced by explosion of Al, Ni, Au, and Pt wires. Some explosions yielded 0.01- μm dia. particles, which agglomerated into spheres having the same density as that of the exploding wire.

They were exploding Al, Zr, Ag, and Pt in SF_6 and found that the relatively inert SF_6 in the EEW permitted producing fluorides of all the metals tested (AlF_3 , ZrF_4 , AgF , PtF_2), as well as sulfur tetrafluoride SF_4 (Cook & Siegel, 1967). The researchers showed also that the product yield increased largely with growing energy injected into the metal. They noted that the yield for exothermic reactions of Al and Zr with F was much higher (98% and 84%) than that for endothermic reactions of Pt and Ag (36% and 27%).

Johnson and Siegel (1970) have been apparently the first to make a setup where a fixed number of tungsten wires (0.76 mm in diameter) were fed automatically. Lengths of wire were inserted beforehand into pockets of a special drum. After every explosion the drum was rotated one step. The wire was fed through the hole of a high-voltage electrode into the interelectrode gap and thus served a switch. This principle of feeding can be used only in production of small batches of powders from hard wires more than 0.5 mm thick.

In Phalen (1972) it was briefly reviewed findings on the use of EEW for production of aerosols and results concerning particles produced for inhalation by explosion of silver wires. From a comparison of published results and his own findings he arrived at the following conclusion. As the capacitor bank voltage rises or the energy injected into the metal increases, the average particle size decreases for all the metals investigated. The particles were always spherical in shape and the particle distribution approached the normal logarithmic one, although bimodal distributions took place as well. Note that all of the aforementioned researchers defined the specific energy w per unit mass of the exploding wire as the capacitor bank energy ($W_0 = 0.5CV_0^2$ with C in μF and V_0 in kV) divided by the mass of the exploding wire. This definition of w is highly erroneous, because it does not take into account the loss in the circuit and the arc, when the explosion

¹As these papers have not been available, I quote these references from (Phalen, 1972).

terminates in an arc discharge. Moreover, the aforementioned researchers analyzed particles, which were either aerosols or precipitates. In either case one did not obtain complete information about the particle size distribution.

Those and many others pioneering studies showed that powders of nearly all metals and various chemical metal compounds could be produced by EEW thanks to the reaction between their vapor and the ambient atmosphere. Moreover, the particle size distribution was found to be similar to the normal logarithmic one with a positive asymmetry, while the characteristic size and the width of the distribution depended on particular parameters of the discharge circuit, the exploding wire, and the environment.

Study of explosion results *versus* explosion conditions

Part of EEW studies were concerned with the search for a more rigorous relationship between the explosion conditions and the energy injected into the wire material.

Conditions were found (Oktay, 1965), when the explosion takes place by the end of the first half-wave of the circuit current (Figure 1c), while the energy W_0 stored in the capacitor bank by that moment is zero. That is, in these conditions W_0 is fully consumed, except the circuit resistance loss, for heating of the exploding wire and the energy is used most efficiently. This EEW regime was called 'matched'. It was found also that the explosion remains to be matched in one and the same circuit if the charging voltage of the capacitor changes in proportion to the wire cross-sectional area. The study of particles, which were produced by explosion of Ag, Cd, and Zn wires in the matched regime (Sherman, 1975), demonstrated that the characteristic diameter d of metal particles was nearly inversely proportional to the injected energy and the character of the ambient gas (in the absence of a chemical reaction) had little effect on d .

Numerous attempts (Oktay, 1965; Bennett, 1969; Sherman, 1977; DiMarco & Burkhardt, 1970; etc.) were made to establish the relationship between the circuit parameters and characteristics of the exploding metal in order to predict the EEW results. Practicable relationships were obtained (Azarkevich, 1973; Azarkevich et al., 1975; Sedoi, 1976) for matched and current-break explosions (Figure 1b and c). Similarity criteria describing main characteristics of explosions

over a wide interval of initial conditions with an error not over 20% satisfying engineering calculation were determined. The boundary between explosions with a current break and arc discharges (Figure 1b and d), conditions of matched explosions, the energy injected to the wire material, the maximum circuit current, the explosion duration, overvoltages arising during explosions, and other characteristics were determined.

The energy W injected to the wire during the first current pulse was found to be

$$W = (h_b W_0 S^2 Z)^{0.5}, \quad (1)$$

where $W_0 = CV_0^2/2$ is the stored energy, J; V_0 is the capacitor charging voltage, kV; $Z = (L/C)^{0.5}$ is the circuit characteristic impedance, Ohm; L is the discharge circuit inductance, μH ; C is the capacitance, μF ; $S = \pi D^2/4$ is the wire cross-sectional area, mm^2 (D being the wire diameter, mm); h_b has the dimensionality of $\text{A}^2\text{s}/\text{mm}^4$ and represents the pre-explosion specific 'action' or thermal toughness of the material heated with a current pulse (Anderson & Neilson, 1959; Cnare & Neilson, 1959; Cnare, 1961). This notion was used earlier (Rudenberg, 1950) for calculation of safety fuses. The obtained h_b values (Anderson & Neilson, 1959; Cnare & Neilson, 1959; Tucker & Neilson, 1959; Cnare, 1961; Kotov et al., 1990) are given in Table 1. It was shown (Chemezova et al., 1998) that h_b varied with the rate of the energy injection to the metal. However, the change was small and h_b values for engineering calculation may be taken from Table 1.

One may see from Eq. (1) that $W = W_0$ at $W_0 = h_b S^2 Z$ if the discharge circuit loss is neglected (the loss does not exceed 5–10% if the design is good). In other words, the relationship

$$W_0 = h_b S^2 Z \quad (2)$$

Table 1. Sublimation energy and 'specific action' of some metals

Metal	W_s (J/mm ³)	h_b , 10 ⁻⁵ (A ² s/mm ⁴)
Cu	47.8	1.95–2.1
Al	33	0.9–1.09
Ag	27.7	1.04
Au	37.7	0.523
Ni	53.9	0.73–0.75
Fe	55.4	0.506
W	92.2	0.8
Pt	58.5	0.945

is a precondition for a ‘matched’ explosion. From Eq. (2) it follows also that if the wire cross-sectional area changes in proportion to the voltage, the explosion remains to be ‘matched’ as was observed earlier (Oktay, 1965; Sherman, 1977). Considering that the particle size decreased in going from Zn to Cd and Ag at an equal density of the injected energy (Sherman, 1977), we suggested that in the general case the particle size depends not on the injected energy, but on the overheat K of the wire material, i.e. the ratio between W and some characteristic energy. The specific energy of sublimation w_s (J/mm^3) was taken as this characteristic energy. The verification of our supposition by the literature data and special experiments on Cu and Al wires (Kotov & Yavorovski, 1978) showed that the particle size decreased linearly with growing overheat of the metal. Considering Eq. (2), the overheat may be expressed as

$$K = W/(w_s S \ell) = (h_b W_0 Z)^{0.5}/w_s \ell, \quad (3)$$

where ℓ is the wire length, mm.

This equation gives the $\ell = \ell_m$ value (ℓ_m being the wire length for a matched explosion) when $K = 1$. It is seen also that if V_0 changes in proportion to ℓ , the overheat will be constant. Consequently, the K value will decrease in proportion to the increase in the wire length, but the explosion will be matched as was observed (Oktay, 1965; Sherman, 1977) at $\ell > \ell_m$.

Since the overheat is inversely proportional to ℓ , one may think that the wire material can be largely overheated if the wire length is decreased. However, quick expansion of the metal leads to the loss of conductivity and cut off of the circuit current. The voltage pulse $V = L(di/dt)$, which arises at the inductance of the discharging circuit, can cause the surface breakdown of the explosion products and the current will be transformed uninterruptedly through the wire material into the arc discharge current (Figure 1d). Therefore, it would be good to know the critical length ℓ_c of the exploding wire, when the current pause is zero and the exploding metal is overheated mostly without the arc discharge, which accompanies the explosion. It was found (Azarkevich et al., 1975; Kotov et al., 1976a,b) that ℓ_c is described by the expression

$$\ell_c[\text{mm}] = B(W_0 D L Z)^{0.36}, \quad (4)$$

where B is the material-dependent dimensional value equal to 27.7 for Al, 18.5 for Cu, and 21 for Ag in terms of the dimensionalities adopted herein. When the

wire length $\ell < \ell_c$, explosions are accompanied by a surface discharge. When $\ell > \ell_c$, explosions occur with a current pause (Figure 1b).

It may be well to know the amplitude of the circuit current when one designs the EEW discharge circuit. The relevant relationships for Cu, Al, and Ag were obtained (Azarkevich, 1973) and analyzed (Chemezova, 1987). It was found that the maximum current in the EEW circuit is determined by the relationship

$$I_M = 0.75 I_0 (h_b S^2 Z / W_0)^{0.25}, \quad (5)$$

where $I_0 = U_0/Z$ is the amplitude of the short-circuit current in the same LC circuit.

Thus, if the circuit parameters L , C , and h_b are known, it is possible to select the V_0 value, the cross-sectional area, and ℓ of the wire providing the required overheat K of the metal.

Engineering calculation of the wire and circuit parameters should take into account several limitations:

1. The calculation error is small if the initial EEW resistance is $R_0 \leq 0.13Z$. If $R_0 > 0.13Z$, the additional factor $B = 0.6(R_0/Z)^{-0.25}$ should be introduced to calculate the EEW current.
2. The obtained relationships are valid when $W_0/(S^2 Z) \leq h_b$, i.e. when the explosion ends during the first half-period of the circuit current.
3. The electronic work function of some metals (Ti, V, Zr, Mo, Ta, W, etc.) is less than their binding energy. As a consequence, even before the binding energy is injected to the metal, the arc discharge caused by an intensive surface emission of electrons sparks over the wire surface and the energy injection to the metal is nearly stopped. Nanopowders of these metals are difficult to produce by the EEW method.

Using these relationships, it is possible to select optimal combinations of the circuit and wire parameters and design a discharge circuit providing the required overheat of the metal and acceptable energy loss.

Preparation of metal nanopowders

Studies into the dependence of the specific surface of powders S_s on the metal overheat showed that the S_s increases linearly with growing K (Kotov & Yavorovski, 1978; Lerner, 1988; Kotov et al., 1997). When the overheat is equal, this S_s is the smaller,

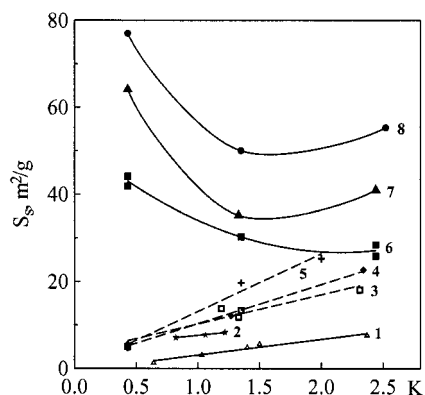


Figure 2. Specific surface of Al_2O_3 , Al, and Cu powders versus overheating of the metal: (1,2) Cu powders produced by EEW with diameter $D = 0.43$ and 0.2 mm respectively; (3,4,5) Al powders produced by EEW with $D = 0.76, 0.45, 0.16$ mm respectively, argon at 10^5 Pa; (6,7,8) Al_2O_3 powders produced by EEW with $D = 0.76, 0.45$ and 0.16 mm in air, respectively.

the larger is the exploding wire diameter (Figure 2, curves 1–5) and the larger is the ambient gas pressure (Glazunov et al., 1978).

The effect of all the aforementioned factors is quite clear. As K increases, the expansion rate accelerates and the degree of ionization of explosion products rises (Chace et al., 1959). Ions probably represent primary condensation centers. Since the vapor supersaturation is high, condensation starts at the very beginning of expansion and progresses at a maximum rate. Therefore, the increase in the expansion rate and the number of condensation centers favors the decrease in the size of particles. When the ambient gas pressure is reduced, the expansion rate of explosion products accelerates too. The initial concentration of vapors diminishes with decreasing diameter of the wire.

The synthesized metal particles have a spherical shape. Their surface is usually smooth, but sometimes there are particles with incomplete coalescence (Figure 3). The particle size distribution approaches the normal logarithmic one with the average geometric deviation $\sigma_g = 1.4$ – 2.2 depending on explosion conditions. However, since the explosion is not uniform, even at $K > 1$ the powder includes particles, which are formed from the liquid phase. Consequently, the distribution curve has a positive asymmetry to the region of micrometer dimensions (Figure 4) and powders require special separation during their production. When the overheat is reduced to $K < 1$, the number of coarse particles increases and the second mode appears in the distribution in the region of micrometer

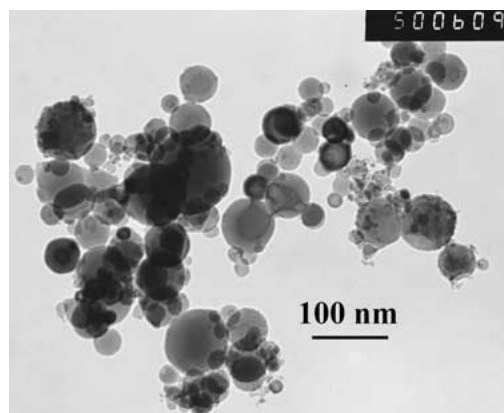


Figure 3. TEM picture of Al particles.

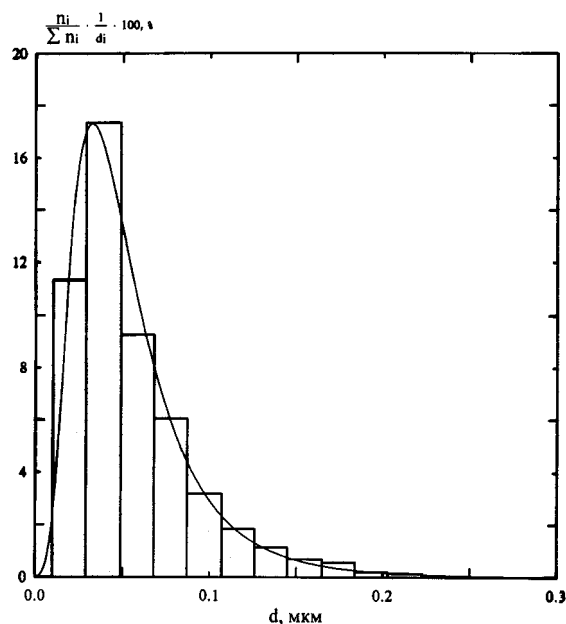


Figure 4. Particle size distribution for Al-powder. Mean geometric diameter is 50 nm, standard geometric deviation 1.8 . Total number of particles 1611 .

dimensions. The powders are weakly agglomerated and are easily dispersed in liquid during ultrasonic treatment.

Purity of the synthesized powders is determined mainly by purity of the exploding wire if the explosion chamber electrodes are made of the same material as the wire.

Considering the spherical shape and a weakly developed surface of the particles, the particle diameter

$d_{\text{BET}} = 6/(S_s \gamma)$ (γ being the density of the particles and S_s the specific surface of the powder) may be appropriately taken as the most objective characteristic dimension.

Inert gases (most frequently argon) are used as the working gas for production of metal nanopowders. However, the synthesized powders are pyrophorous and catch fire when they are taken out to air. For this reason, the powders must be preserved with the working gas or liquids, which do not contain oxygen, for example, hexane. For convenience, in the analysis of some characteristics and in certain applications, one may use passivation of the powder surface by a slow (usually for 12 h or longer) inleakage of air to the installation. In this case, a dense oxide film ~ 2 nm thick is formed on Al particles and they are oxidized slowly when kept in air. Copper powders with $S_s \geq 10$ m²/g ($d_{\text{BET}} \leq 65$ nm) contain ~ 1 wt % oxide after passivation. However, when the powders are kept in air, they are oxidized rather vigorously. Spherical particles are broken and form CuO agglomerates whose specific surface is 3 times as large as the initial surface (Figure 5) (Kotov et al., 2003c). Powders containing almost 100% CuO may be obtained in this way. Explosions of alloy wires provide nanoparticles of the corresponding alloy. When wires made of different metals are exploded simultaneously, mixtures of particles of the initial metals and their compounds are produced. The mass ratio of these components can be varied over broad limits (Azarkevich et al., 1997; Kotov et al., 2003a) by changing explosion conditions. When Al and Fe wires were exploded simultaneously, the concentration of metastable γ -Fe could account for up to 60 wt % of the total amount of iron in the powder.

Studies showed that in non-equilibrium EEW conditions the structure of metal particles may be imperfect (Figure 5a) and include various microdistortions (dislocations, twins, and inhomogeneities). Moreover, a considerable quantity of metastable phases is fixed in particles at normal temperature. For example, γ -Fe and β -W were produced during explosion of Fe and W (Yavorovski, 1981).

The production of metal powders < 50 nm in size with productivity $f \geq 50$ g/h is hampered by the need to use wires with $D < 0.3$ mm. This starting material is relatively expensive and the continuous feed of the wire to the explosion chamber is difficult to realize because of its low mechanical strength.

For particles with $d_{\text{BET}} = 50$ –100 nm, the output of different metals is 50–200 g/h at the power consumption of 50–25 kWh/kg. However, as the output increases and, especially, exceeds 100 g/h, problems arise in connection with a strong agglomeration and coalescence of particles because of their high concentration in the working gas flow and a decrease in the quenching rate.

Thus, the EEW method allows making nanopowders of various metals, alloys and chemical compounds of metals at a sufficiently high productivity. The characteristic size of particles may be adjusted between ~ 20 nm and tens of micrometers by changing explosion conditions.

Production of metal oxide powders

As was mentioned above, the pioneering papers noted that explosion of reactive metals in air leads to formation of oxide nanoparticles. Later studies established

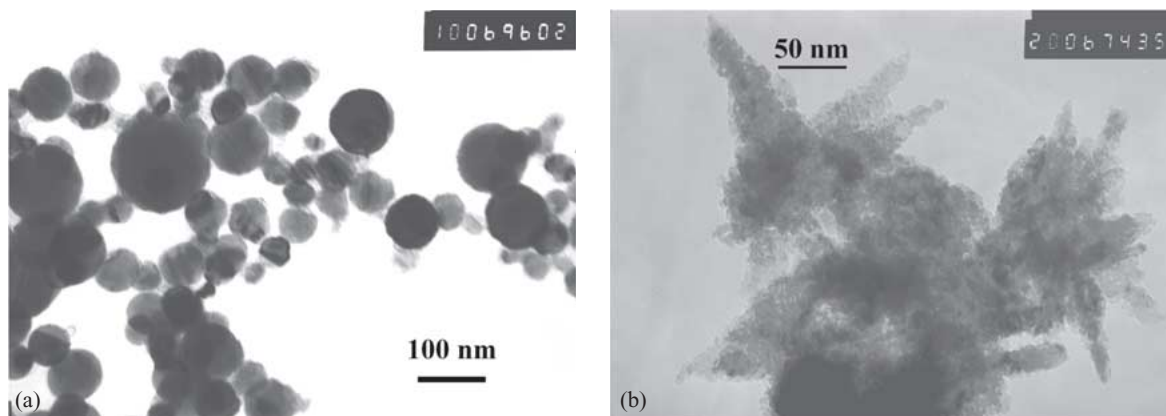


Figure 5. TEM picture Cu powders after preparation (a) and 1.5-year storage in air (b).

dependences of the specific surface of Al_2O_3 powders and the degree of the metal oxidation on the concentration of oxygen in its argon mixture (Lerner, 1988), the overheat of the metal exploded in air (Kotov et al., 1997), the pressure and the concentration of oxygen in its nitrogen mixture (Kotov et al., 1999).

It was found that at the overheat $K \geq 1$ in air and the concentration of $\text{O}_2 \geq 20$ vol. % in its mixture with an inert gas the degree of oxidation reaches 100% and the specific surface of the powder is 2–2.5 times larger than the specific surface of metal powders synthesized under similar conditions (Figure 2, $K > 1$). It was assumed (Kotov & Samatov, 1994) that particles of oxides of reactive metals, such as Al, Ti, Zr, Fe, etc. (Table 2), whose oxidation energy is higher or approaches the sublimation energy, are formed partially at the expense of the oxidation energy during evaporation of metal particles, which appeared earlier. Since explosion products expand as a cylinder, whose density is much larger than the density of the working gas, oxidation can take place only on the surface of this cylinder, while metal particles are condensed and formed inside the cylinder. The last processes cause a decrease in the vapor concentration. Oxygen penetrates inside the cylinder of explosion products and brings about the process of burning and evaporation of the formed metal particles and subsequent condensation of the vapors to form oxide particles. Since the vapor concentration is lower and the melting point of oxides is much higher than the corresponding values of metals, the size of oxide particles proves to be much smaller (Figure 2, $K > 1$).

We verified this supposition for Al_2O_3 (Kotov et al., 1997; 1999), TiO_2 and ZrO_2 (Kotov et al., 1996), MgAl_2O_x (Kotov et al., 1999), and $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$ (Azarkevich et al., 2001) nanopowders, which were produced when the energy injected to the metal was a

little higher than the energy corresponding to the boiling start point. It was found that in these conditions the wires disintegrated to micrometer-sized particles burning during their scatter in the oxidizing gas and leaving behind a vapor tail where the oxide nanoparticles were formed. Thanks to the decrease in the vapor concentration of the explosion chamber, it was possible to increase the specific surface of powders to 80–100 m^2/g , i.e. decrease the particle size d_{BET} to 15–20 nm at no sacrifice of the production rate or the rise of the energy consumption (Figure 2, curves 6–8 at $K < 1$). When the burning process is delayed, the specific surface of the oxide powders may be adjusted over broad limits thanks to the decrease in the oxygen concentration and, hence, the increase in the scatter speed of particles (Kotov et al., 1999).

Of course, in this case the powder represents a mixture of residual micrometer-sized particles and nanoparticles (Figure 6). However, special separating systems allow extracting up to 30 wt % nanoparticles. Since the exploding wire has a larger mass ($K < 1$), the production rate is 100–200 g/h of the nanofraction at the same energy consumption. Coarse particles may be used, for example, as the starting material for the target in production of nanopowders having a complicated composition by the method of laser evaporation (Kotov et al., 2002).

On the other hand, explosion of copper in air or a nitrogen–oxygen mixture provides particles whose size is a little smaller than the size of particles in powders of metal copper prepared under similar conditions in an inert gas (Lerner, 1988; Azarkevich et al., 2003).

From Table 2 it is seen that the oxidation energy of Cu accounts for less than 0.5 of the sublimation energy. Consequently, the aforementioned process of secondary evaporation is nearly absent. An insignificant decrease in the particle size in this case is probably due to the delay of full condensation, because the temperature of explosion products is maintained for a long time by the released oxidation energy. The particle size may be decreased only by increasing the overheat, decreasing the wire diameter, and reducing the ambient gas pressure as for metal powders.

A situation, which is intermediate between those described above, is observed for oxide powders of Ni (Kotov et al., 2003b) having the oxidation energy $0.66w_s$ (Table 2). In this case, burning takes place, but, probably, stops quickly, because the working gas cools the scattered particles. As a result, at $K < 1$ the yield of the NiO nanopowder does not exceed 15 wt % (S_s

Table 2. Sublimation and oxidation energies for some metals

Metal	w_s (J/g)	w_{ox} of metal (J/g)
Cu	5353	2551 (CuO) 1364 (Cu ₂ O)
Al	11550	30700
Ti	8755	19700
Zr	9215	12000
Fe	7480	7390 (Fe ₂ O ₃) 6680 (Fe ₃ O ₄)
Ni	6056	4000

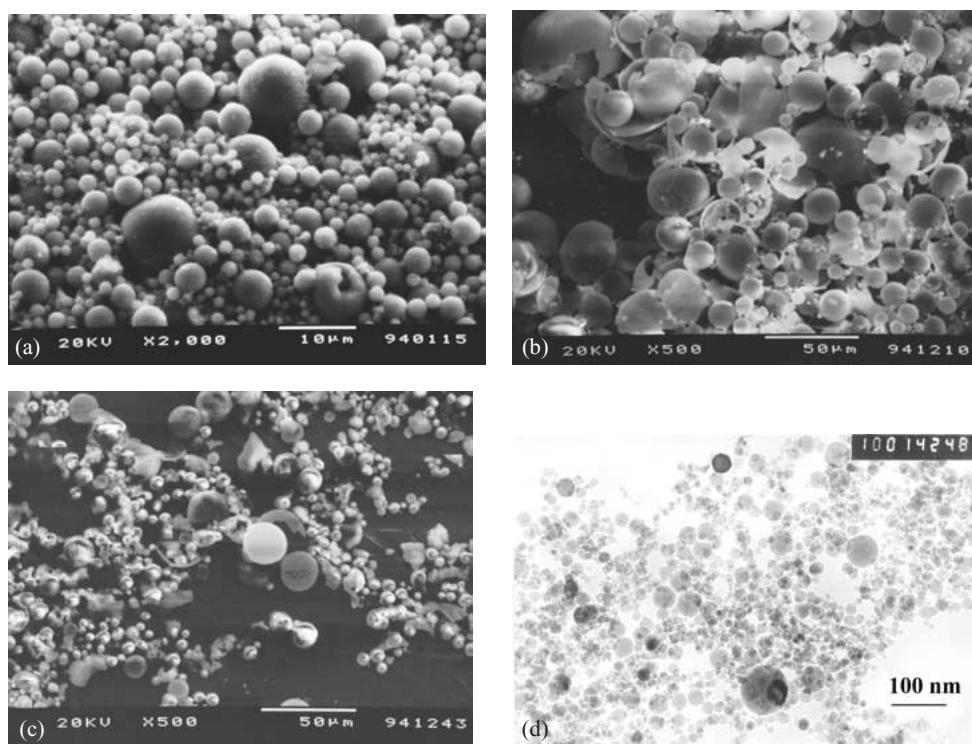


Figure 6. Large particles of TiO_2 (a), ZrO_2 (b), and Al_2O_3 (c) are separated from fine particles, when $K = 0.4$. Fine particles of Al_2O_3 (d) are separated from large particles when $K = 0.4$.

up to $60 \text{ m}^2/\text{g}$). At $K > 1$ the yield rises to 30 wt %, but S_s diminishes to $\sim 15 \text{ m}^2/\text{g}$.

Thus, EEW made of reactive metals (the oxidation energy exceeds the sublimation energy) provides powders of corresponding oxides whose specific surface is several times larger than the specific surface of metal powders prepared using the same overheat, wire diameter, and working gas pressure. The S_s value may be increased additionally thanks to burning of scattered boiling droplets of the metal.

The oxide particles have a nearly spherical shape and a relatively smooth surface. However, both spherical and cubic particles were observed for nickel oxides. The oxide powders have diverse phase compositions. The Al oxide always contains γ and δ - Al_2O_3 . Their ratio changes with explosion conditions. ZrO_2 powders include up to 70% of the tetragonal phase in addition to the monoclinic phase. Note that the metastable tetragonal ZrO_2 phase is rather stable. When the powder is heated to 1000°C and is allowed to stand for 1 h, about 15 wt % tetragonal phase remains in the powder. TiO_2 powders contain both rutile and anatase. The concentration of the latter grows with decreasing size

of particles. Oxide powders are weakly agglomerated, have a low bulk weight, are poorly compactable, and contain up to 7 wt % of sorbed gases and moisture, most of which are removed by heating to $\sim 300^\circ\text{C}$. The powders preserve their composition and characteristics during storage under standard laboratory conditions.

MgAl_2O_3 was produced from the AlMg alloy (~ 1.3 wt % Mg). The content of the low-temperature γ -phase in the MgAl_2O_x powder was much higher than in Al_2O_3 . It is noteworthy that although Al_2O_3 and MgAl_2O_3 powders were produced under similar conditions, addition of 1.3 wt % Mg did not lead to appearance of MgAl_2O_4 or MgO compounds. Probably, Mg atoms were located in the Al_2O_3 lattice. The MgAl_2O_4 structure appeared only in the ceramics sintered from this powder (Ivanov et al., 1999).

It should be noted that systematic studies concerned with production of nanopowders of other chemical compounds by the EEW method have not been performed in Russia so far. An exception is the study (Lerner, 1988), in which Al wires were exploded in nitrogen at a pressure up to 1.5 MPa to prepare $\text{Al}+\text{AlN}$ powders containing up to 90 wt % AlN. The specific

surface of the particles was $\sim 20 \text{ m}^2/\text{g}$. The AlN concentration decreased to 80 wt% as the pressure was reduced to 10^5 Pa . The last result was confirmed by Kotov and Samatov (1999). In addition, those studies showed that the use of ammonia (NH_3) mixed with 80 vol. % N_2 at 10^5 Pa allows increasing the AlN concentration probably to 100% with particles $\sim 30 \text{ nm}$ in size ($S_s = 50 \text{ m}^2/\text{g}$). However, these studies have not been extended owing to the lack of interest for AlN powders.

Equipment and production technology of powders

After a long-term work on development and tests of installations for preparation of nanopowders by the EEW method, we have come to the conclusion that metal and oxide powders can be expediently produced in similar installations, in which some units are replaced when we move from metals to oxides. It is necessary to note the following. When one needs to prepare metal or alloy nanopowders, the working gas is inert. However, if the metal/alloy does not form compounds with nitrogen, nitrogen is preferable since it has a higher electrical strength. When oxide nanopowders are prepared, it is possible to use a mixture of nitrogen and argon with oxygen.

The functional block diagram of the facility is shown in Figure 7. Its operating principle is as follows. The high-voltage charging device 1 continuously charges capacitors of the pulsed current generator 2. The wire 15 is continuously fed by the wire feeding mechanism 4 to the explosion chamber 3. When the wire reaches the high-voltage electrode 20, the wire length sensor of the wire feeding mechanism generates

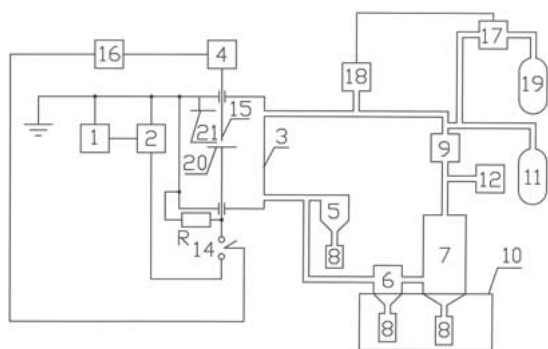


Figure 7. Functional block diagram of the installation for producing nanopowders by EEW method.

a signal to the switch triggering unit 16. A high-voltage pulse from the unit 16 is applied to the intermediate electrode of the three-electrode gas switch 14 and initiates a discharge between the main electrodes of the switch 14. The capacitors 2 discharge through the wire 15. A strong current pulse passing through the wire causes its heating and explosion. The fan 9 circulates the working gas, which carries the produced powder sequentially through the trap 5, the cyclone 6, the electric and mechanical cloth filters 7. The powder settles down in hoppers 8 of the aforementioned units. Coarsest powder particles are collected in the trap 5 and finest powder particles are caught in the filters. Upon passing the cloth filter, the working gas is returned to the explosion chamber. When oxides are prepared, oxygen is taken from the working gas during each explosion. The oxygen sensor 18 is installed in the facility. The sensor checks the oxygen concentration in the working gas and controls the electric motor driving the oxygen flow governor 17. In this way the oxygen concentration in the facility volume is maintained at a desired level. Before the work, the facility volume is evacuated to a pressure of 50 Pa using the vacuum pump 12. Nitrogen and oxygen are poured into the facility in the required ratio to a preset pressure. Nitrogen is fed from the bottle 11 and oxygen is supplied from the bottle 19 with the help of the flow governor 17.

To ensure safety of the attending personnel and preclude contamination of the ready powder, it is unloaded, preserved, and packed in the sealed box 10.

A wire 0.3–0.8 mm in diameter and 30–250 mm long is used usually. The explosion repetition frequency is up to 1 Hz. The charging voltage of the capacitors is up to 40 kV, while the capacitor bank is rated at 2–4 μF . The production rate is 50–100 g/h of metal nanopowders and 100–200 g/h of oxide nanopowders at the power consumption of 5 kW or smaller.

The use of nanopowders

Synthesized powders were used in the following applications.

Chemically and wear resistant ceramics were developed (Ivanov et al., 1995; 1999; 2001). Ceramics based on MgAl_2O_4 had the microhardness up to 24 GPa and the density accounting for 0.98 of the theoretical value with grains 110–300 nm in size.

Samples of a metal–matrix material were prepared on the basis of Al and Cu nanopowders and SiC powders. It was shown that electromagnetic pulsed pressing

(Kotov et al., 2000a; Popov et al., 2002) ensured good wettability of SiC particles with aluminum or copper without additional thermal treatment. The density of the material approached the theoretical value.

The bending strength under 4-point loading of composite ceramics based on Al₂O₃ and ZrO₂ was 500 MPa. The ceramic had nearly theoretical density with grains 140 and 70 nm in size for Al₂O₃ and ZrO₂, respectively (Ivanov et al., 2000).

Dynamic compaction of passivated Al nanopowders (Rhee et al., 2003) provided samples of a metal–matrix material, in which fragments of the broken oxide film served as reinforcement elements of the aluminum matrix. The material had a high strength at temperatures up to 300°C.

The Al₂O₃ powder as the matrix and micrometer-sized particles of a stainless steel were used for creation of a composite material for plasma cathodes used in nanosecond frequency electron accelerators (Kotov et al., 2000b). The cathode characteristics did not change after over 10⁸ pulses having the repetition frequency up to 200 Hz.

In all these examples, the dynamic electromagnetic compaction provided compacts whose density accounted for 0.7–0.85 of the theoretical value, which ensured a relatively small growth of grains during standard synthesis of ceramic materials at much lower temperatures.

Conclusion

Thus, the reviewed studies, which have been performed by different researchers and teams, allowed developing a method for production of nanopowders, which employs the phenomenon of EEW. From the available data it is possible to calculate a wide range of explosion conditions for production of nanopowders of metals, alloys and their chemical compounds. Although synthesized powders have a wide particle size distribution, they successfully solve some problems in production of materials with improved characteristics. The EEW method is ecologically safe, provides a sufficiently high production rate, requires a relatively small energy, and allows making powders with a small degree of contamination.

Acknowledgements

The author is thankful to his colleagues with whom he has managed to achieve some success in the study

of electric explosion and development of equipment for production of nanopowders. Also, the author is grateful to ISTC and INCO-COPERNICUS Fund for their financial support, which facilitated the studies described above.

References

- Anderson G.W. & E.W. Neilson, 1959. Use of the action integral in exploding wire studies. In: Chace W.G. and More H.K. eds. *Exploding Wires*, Vol. 1. Proc. of 1st Conf. on the Exploding Wire Phenomenon, Boston, USA, 24–27 March 1959. Plenum Press, New York, pp. 97–103.
- Azarkevich E.I., 1973. Using similarity theory for calculating some characteristics of EEW. *Zh. Sov. Techn. Fiz.* 43, 141–145 (in Russ.).
- Azarkevich, E.I., Y.A. Kotov & V.S. Sedoi, 1975. Conditions of current pause appearance at EE. *Zh. Sov. Techn. Fiz.* 45, 175–177 (in Russ.).
- Azarkevich E.I., A.P. Ilyin, D.V. Tikhonov & G.V. Yablunovskii, 1997. Electric explosion sintering ultrafine powders of alloys and intermetallics. *Zh. Russ. Fiz. Chem. Mater. Treatment* 4, 85–88 (in Russ.).
- Azarkevich E.I., I.V. Beketov & Y.A. Kotov, 2001. Producing iron oxide powders with specific surface up to 100 m²/g by EEW method. In: Kotov Y.A., Petrunin V.F. and Ivanov V.V. eds, *Proc. of 5th Russian conf. 'Phys. and Chemistry of Ultrafine Systems'*, Part 1, Ekaterinburg, Russia, 9–13 October 2000, pp. 93–95 (in Russ.).
- Azarkevich E.I., Yu.A. Kotov & A.I. Medvedev, 2003. Preparing Cu-oxide powders by EEW method. In: Alymov M.I., Yu.V. Petrikin and V.F. Petrunin eds, *Proc. of 6th Russian Conf. 'Phys. and Chemistry of Ultrafine (Nano-) Systems'*, 19–23 August, 2002, Tomsk, Russia, Moscow, MEPI, 114–117 (in Russ.).
- Bennett F.D., 1969. High-temperature exploding wires. In: Rouse C.A. ed. *Collected papers: Progress in high-temperature physics and chemistry*. New York, Pergamon Press, pp. 2–63.
- Chace W.G., 1959. A brief survey of exploding wire research. In: Chace W.G. and More H.K. eds. *Exploding Wires*, Vol. 1. Proc. of 1st Conf. on the Exploding Wire Phenomenon, Boston, USA 24–27 March 1959, Plenum Press, New York, pp. 7–13.
- Chace W.G., R.L. Morgan & K.R. Saari, 1959. Conductivity during the 'dwell-time' of a wire explosion. In: Chace W.G. and More H.K. eds. *Exploding Wires*, Vol. 1. Proc. of 1st Conf. on the Exploding Wire Phenomenon, Boston, USA, 24–27 March 1959, Plenum Press, New York, pp. 59–72.
- Chemezova L.I., 1987. Modeling and engineering calculation of EEW of various metals. Ph.D., Inst. of High Current Electronics, Tomsk, Russia (in Russ.).
- Chemezova L.I., G.A. Mesyats, V.S. Sedoi, B.N. Semin & V.V. Valevich, 1998. Proc. of 28 Int. Symp. on Discharges and Electric Insulation in Vacuum. Vol. 1, Endhoven, Netherlands, 17–21 August 1998, Hosted by Endhov. *Univers. of Technology*, pp. 48–51.
- Cnare E.C., 1961. Observations on the striations of electrically exploded copper foils. *J. Appl. Phys.* 32, 1043–1044.

- Cnare E.C. & F.W. Neilson, 1959. Large exploding wires—correlation to small wires and pause time *versus* length dependency. In: Chace W.G. and More H.K. eds. *Exploding Wires*, Vol. 1. Proc. of 1st Conf. on the Exploding Wire Phenomenon, Boston, USA 24–27 March 1959, Plenum Press, New York, pp. 83–96.
- Cook E. & B. Siegel, 1967. Reactions of SF₆ with exploding metals. *J. Inorg. Nucl. Chem.* 29, 2739–2743.
- DiMarco J.N. & L.C. Burkhardt, 1970. Characteristics of a magnetic energy storage system using exploding foils. *J. Appl. Phys.* 41, 3894–3899.
- Glazunov G.P., V.P. Kantsedal & A.A. Kornienko, 1978. Some properties of fine powders prepared by EEW in high pressure gas. *Zh. Sov. Questions Atom. Sci. Technic. Atom. Mater. Sci.* 1, 21–24 (in Russ.).
- Ivanov V.V., Y.A. Kotov, V.R. Khrustov, O.M. Samatov, R. Bohme, H. Karow & G. Schumacher, 1995. Synthesis and dynamic composition of ceramic nanopowders by techniques based on electric pulsed power. *J. Nanostr. Mater.* 6, 287–290.
- Ivanov V.V., S.N. Pararin, V.R. Khrustov & A.I. Medvedev, 1999. Fabrication of articles of nanostructured ceramics based on Al₂O₃ and ZrO₂ by pulsed magnetic compaction and sintering. In: Vincenzini P. ed. Proc. of 9th Cimtec-World Ceramic Congress, Ceramics: Getting into the 2000's, Part C. Florence, Italy, 14–19 June, 1998. Techna, Faenza, pp. 441–448.
- Ivanov V.V., Y.A. Kotov, V.R. Khrustov, O.M. Samatov, S.Y. Ivin, A.M. Murzakaev, V.V. Osipov, M.G. Ivanov, A.K. Stoltz & A.I. Medvedev, 2000. Development of Al₂O₃–ZrO₂ nanostructured composites using pulsed power technologies. In: Ruehle M. and Gleiter H. eds. *Interface Controlled Materials*, EUROMAT99-Vol. 9, Wiley, pp. 166–171.
- Ivanov V.V., S.Y. Ivin, A.I. Medvedev, S.N. Pararin, V.R. Khrustov & A.K. Stoltz, 2001. Peculiarities of sintering ceramic on base of doped MgO and TiO₂ of α -Al₂O₃ with submicron structure. *Russ. J. Inorg. Mater.* 37, 248–256.
- Johnson R.L. & B.A. Siegel, 1970. Chemical reactor utilizing successive multiple electrical explosion of metal wires. *Rew. Sci. Instr.* 41, 854–859.
- Joncich M.J. & D.C. Reu, 1964. Synthesis of inorganic binary compounds using exploding wire techniques. In: Chace W.G. and More H.K. eds. *Exploding Wires*, Vol. 3. Proc. of the 3rd Conf. on Exploding Wire Phenomenon. Boston, USA, 10–12 March 1964, Plenum Press, New York, pp. 353–359.
- Joncich M.J., J.W. Vauchn & B.F. Kuntsen, 1966. Preparation of metal nitrides by the exploding wire technique. *Canad. J. Chem.* 44, 137–142.
- Karioris F.G. & B.R. Fish, 1962. An exploding wire aerosol generator. *J. Col. Sci.*, 17: 155–161.
- Kotov Y.A. & N.A. Yavorovski, 1978. Investigation of particles preparing by electrical explosion of wires. *Zh. Sov. Phys. Chem. Mater. Treatment* 4, 24–29 (in Russ.).
- Kotov Y.A. & A.P. Tsiplenko, 1984. Research of explosive opening switch having dielectric cumulative jets. In: Titov V.M. and Shvetsov G.A. eds. *Ultrahigh Magnetic Fields*, Proc. of 3rd Int. Conf. on Megagauss Magnetic Fields, Generation and Related Topics, Novosibirsk, Russia. 13–17 June 1983, Moscow, Nauka, pp. 402–405 (in Russ.).
- Kotov Yu.A. & O.M. Samatov, 1994. Characteristics of alumina powders prepared by pulsed heating of wire. *Russian J. Poverkhnost*, 10-11, 90–94 (in Russ.).
- Kotov Y.A. & O.M. Samatov, 1999. Production of Nanometer-Sized AlN powders by the Exploding Wire Method. *J. NanoStruc. Mater.* 12, 119–122.
- Kotov Y.A., B.M. Kovaltchuk, N.G. Kolganov, G.A. Mesyats & V.S. Sedoi, 1976a. Nanosecond pulse generators with inductive storage. In: Proc. of 1st IEEE Int. Pulsed Power Confer. Lubbock, Texas, USA, 9–11 November 1976, pp. 1A1–1A11.
- Kotov Y.A., V.S. Sedoi & L.I. Chemezova, 1976b. Energetic-time characteristics of LC-circuit with EEW. In: Mesyats G.A. ed. *Collected Papers: Development and Application of Intensive Electron Beams*. Novosibirsk, Nauka, pp. 61–69 (in Russ.).
- Kotov Y.A., O.M. Samatov, V.S. Sedoi, L.I. Chemezova & A.A. Chertov, 1990. Heating of conductors by high-density current. The energy input and the integral of action. In: Titov V.M. and Shvetsov G.A. eds. *Proc. of 5th Int. Conf. on Megagauss Fields and Pulsed Power Systems*, Novosibirsk, Russia, 3–7 July 1989, Nova Science Pub. New York, 1990, pp. 497–502.
- Kotov Y.A., I.V. Beketov, A.M. Murzakaev, O.M. Samatov, R. Boehme & G. Schumacher, 1996. Synthesis of Al₂O₃, TiO₂ and ZrO₂ nanopowders by electrical explosion of wires. In: Schulz R. ed. *Proc. of Symp. Metastable, Mechanically Alloyed and Nanocrystalline Materials – ISMANAM-95*, Quebec, Canada, 24–28 July 1995, Material Science Forum Vols. 225–227, Transtec Publications, Switzerland, pp. 913–916.
- Kotov Y.A., E.I. Azarkevich, I.V. Beketov, T.M. Demina, A.M. Murzakaev & O.M. Samatov, 1997. Producing Al and Al₂O₃ nanopowders by electrical explosion of wire. In: Abelard P., Boussuge M., Chartier Th., Fantozzi G., Lozes G. and Rousset A. eds. *Proc. of 5th Conf. and Exhibition of the European Ceramic Society*, Versailles, France, 22–26 June, 1997, *Key Engineering Materials*, Vol. 132–136, Part 1. Trans Tech. Publications, Switzerland, pp. 173–176.
- Kotov Y.A., I.V. Beketov, E.I. Azarkevich & A.M. Murzakaev, 1999. Synthesis of nanometer-sized powders of alumina containing magnesia. In: Vincenzini P. ed. *Proc. of 9th Cimtec-World Ceramic Congress, Ceramics: Getting into the 2000's*, Part B. Florence, Italy, 14–19 June 1998. Techna, Faenza, pp. 277–284.
- Kotov Y.A., V.A. Popov, I.V. Beketov, O.M. Samatov, V.V. Ivanov, S.N. Pararin, Y.E. Markushkin & V.V. Garlevskij, 2000a. Using nano-materials for producing aluminum matrix composites. In: Chandra T., Higashi K., Suayanarayana C. and Tome C. eds. *Proc. Int. Conf. on Processing & Manufacturing of Advance Materials – THERMEC2000*. Las-Vegas, USA, 4–8 December 2000, F09-03POF.
- Kotov Y.A., E.A. Litvinov, S.Y. Sokovnin, M.E. Balezin & V.R. Khrustov, 2000b. Metalloceramic cathodes for electron accelerators. *Dokl. Phys.* 45, 18–21.
- Kotov Y.A., V.V. Osipov, M.G. Ivanov, O.M. Samatov, V.V. Platonov, E.I. Azarkevich, A.M. Murzakaev & A.I. Medvedev, 2002. Properties of oxide nanopowders prepared by target evaporation with a pulse-periodic CO₂ laser. *J. Tech. Phys.* 47, 1420–1426 (Trans. from Russian *Zh. Tekn. Fiz.* 2002, 72: 76–82).
- Kotov Y.A., O.M. Samatov, Ch.K. Rhee, A.M. Murzakaev, O.R. Timoshenkova, A.I. Medvedev & A.K. Shtolts, 2003a. Nanopowders prepared by simultaneous electrical explosion of Al and Fe wires. *Proc. of 10th APAM Topical Seminar and 3rd*

- Conf. 'Materials of Siberia, Nanoscience and Technology', 2–6 June, 2003, Novosibirsk, Russia. Instit. Inorg. Chemistry of Siberian Division of RAS, Novosibirsk, 128–130.
- Kotov Yu.A., I.V. Beketov, A.V. Bagazeev, A.M. Murzakaev, A.I. Medvedev & O.M. Samatov, 2003b. Properties NiO powders prepared by EEW method. In: Alymov M.I., Yu.V. Petrikin and V.F. Petrunin eds, Proc. of 6th Russian Conf. 'Phys. and Chemistry of Ultrafine (Nano-) Systems', 19–23 August, 2002, Tomsk, Russia, Moscow, MEPI, 158–156 (in Russ.).
- Kotov Yu.A., Ch.K. Rhee, A.V. Bagazeev, I.V. Beketov, T.M. Demina, A.M. Murzakaev, O.M. Samatov, O.P. Timoshenkova, A.I. Medvedev & A.K. Shtolts, 2003c. Production of nanopowders by electrical explosion of wires: A study of their oxidation during storage and heating in air. In: Ahn J.-H. & Hahn Y.-D. eds. Proc. of the ninth Int. Symp. on Metastable, mechanically alloyed and nanocrystalline materials. Seoul, Korea, 8–12 September, 2002, J. of Metastable and Nanocrystalline Materials. Trans Tech. Publ., Switzerland, 15–16, 343–348.
- Leopold H.S., 1964. Effect bridgewire parameters on explosive initiation. In: Chace W.G. and More H.K. eds. Exploding Wires, Vol. 3. Proc. of the 3rd Conf. on Exploding Wire Phenomenon, Boston, USA, 10–12 March 1964, Plenum Press, New York, pp. 125–152.
- Lerner M.I., 1988. Operating by formation process of particles in EEW conditions. Ph.D., Inst. of High Voltages. Tomsk, Russia (in Russ.).
- McFarlane H.B., 1959. A high voltage, quick-acting fuse, to protect capacitor bank. In: Chace W.G. and More H.K. eds. Exploding Wires, Vol. 1. Proc. of the 1st Conf. on Exploding Wire Phenomenon. Boston, USA, 24–27 March 1959, pp. 324–344.
- Oktay E., 1965. Effect of wire cross section on the first pulse of an exploding wire. Rev. Sci. Instr. 36, 1327–1328.
- Phalen R.F., 1972. Evaluation of an exploded-wire aerosol generator for use in inhalation studies. Aerosol Sci. 3, 395–406.
- Popov V.V., D.R. Lesuer, Y.A. Kotov, V.V. Ivanov, O.M. Smirnov, A.V. Marmulev, S.V. Zayats & I.V. Beketov, 2002. On the development of MMCs containing copper with silicon carbide reinforcement using nanomaterials and dynamic compaction. Proc. of IX Int. Conf. on Composites Engineering, San Diego, California, USA, 1–6 July 2002, pp. 627–628.
- Rhee C.K., G.H. Lee, W.W. Kim, V.V. Ivanov, S.V. Zayats & A.I. Medvedev, 2003. Nanostructured Al/Al₂O₃ composite sintered by magnetic pulse compaction. J. Metastable Nanocrystals 15–16, 401–406.
- Rüdenberg R., 1950. Transient Performance of Electric Power Systems. New York-Toronto-London, 678 pp.
- Sedoi V.S., 1976. Some regularities of EEW. Zh. Sov. Tech. Fiz. 46, 1707–1710 (in Russ.).
- Sherman P.M., 1975. Generation of submicron metal particles. J. Colloid Interface Sci. 51, 87–93.
- Sherman P.M., 1977. Prediction of conditions for a single pulse discharge. J. Appl. Phys. 48, 143–144.
- Tucker T.J. & F.W. Neilson, 1959. The electrical behavior of fine wires exploded by a coaxial cable discharge system. In: Chace W.G. and More H.K. eds. Exploding wires, Vol. 1. Proc. of 1st Conf. on the Exploding Wire Phenomenon, Boston, USA, 24–27 March, 1959, Plenum Press, New York, pp. 73–81.
- Vanyukov M.P. & V.I. Isaenko, 1962. Investigation of light produced by exploding wires. Zh. Sov. Tech. Fiz. 32, 197–201 (in Russ.).
- Yavorovski N.A., 1981. Electrical explosion of wires as method for preparation of ultrafine metal powders. Ph.D., Inst. of High Voltages, Tomsk, Russia (in Russ.).