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SYNTHESIS OF Al–Al_2O_3 AND Al–AlN NANOPARTICLE COMPOSITES VIA ELECTRIC EXPLOSION OF WIRES

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Composite Al–Al_2O_3 *and* Al–AlN *nanoparticles were synthesized via electric explosion of aluminum wires in an argon–oxygen gas mixture and in nitrogen. The parameters of electric explosion and gas medium affect the size and relative content of nitride and aluminum oxide in the nanoparticles. Processes of forming chemical compounds during aluminum oxidation at the contact surface between explosive products and gas and of nitrogen diffusions into the nanoparticles of the condensed phase are considered.*

Keywords: electric explosion of wires, nanoparticles, aluminum, aluminum nitride, aluminum oxide.

INTRODUCTION

A perspective method for synthesis of nanoparticles of metals and chemical compounds (oxides and nitrides) is electric explosion of wires (EEW). EEW is the process with high rates of change of the thermodynamic system parameters observed when the current with density 10^6–10^9 A/cm^2 runs through a metal wire. The processes of conversion of the wire metal from the condensed state into the two-phase state (liquid metal – gas/plasma) [1, 2] develops intensively for current densities in the range 10^7–10^8 A/cm^2.

In [3] it was shown that aluminum (Al), aluminum oxide (Al_2O_3), and aluminum – aluminum nitride (Al–AlN) composite nanoparticles can be synthesized via electric explosion of an aluminum wire in argon, air, and nitrogen atmosphere. In particular, it was established that the size of Al, Al_2O_3, and AlN nanoparticles is determined by the amount of overheat of the wire metal. From the data presented in [3] it follows that with decreasing amount of overheat, the specific surface of Al_2O_3 powders increases. It is demonstrated that the small fraction of nanopowders synthesized at a nitrogen pressure of 0.3 MPa and amount of overheat $>1.7E_c$ (here E_C is the aluminum sublimation energy) has a specific surface of about 30 m^2/g and AlN content exceeding 95 mass%.

The Al–AlN and Al nanoparticles are used as precursors for low-dimensional nanostructures (nanosheets) of pseudoboehmite used to develop biologically active materials [4]. Analogous structures are produced in the reaction of AlN nanoparticles with water [5]. Moreover, the rate of forming nanosheets during oxidation of Al–AlN nanoparticles with water is determined by the content of the AlN phase.

The aluminum nanoparticles represent composite structures with the core-shell morphology, where the core is metal aluminum and the shell is amorphous aluminum oxide (Al–Al_2O_3) [6]. In the process of oxidation of aluminum nanoparticles with water, hollow spheres are formed coated by pseudoboehmite nanosheets [7]. The thickness of the aluminum oxide layer can determine the rate of aluminum oxidation and the morphology of hollow spheres coated by pseudoboehmite nanosheets. Because of their biological activity, nanostructures with similar morphology can be used as containers for bioactive substances.

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It is obvious that the properties of the Al–AlN and Al–Al_2O_3 nanoparticles are determined by the conditions of their synthesis via EEW [8]. In [3] it has already been shown that oxygen additives to the working gas of the setup intended for synthesis of aluminum powder allows amorphous oxide coating to be formed on particles being synthesized. This allows agglomeration of aluminum particles to be reduced and the particle surface to be protected from oxidation.

This suggests that the content of oxide and nitride phases on the nanoparticle surface can be regulated by changing the amount of overheat of aluminum wires, the pressure, and the active gas concentration during electric explosion, thereby allowing low-dimensional nanostructures with predetermined properties to be synthesized. In addition, a study of synthesis of AlN and Al_2O_3 nanoparticles having numerous practical applications is of special interest.

The present work is aimed at elucidation of conditions of electric explosion of an aluminum wire allowing aluminum nanoparticles with predetermined AlN and Al_2O_3 contents to be synthesized.

EXPERIMENTAL PROCEDURE

Aluminum nitride and aluminum oxide nanoparticles were synthesized in the nitrogen (N_2) atmosphere and in the mixture of argon and oxygen ($Ar + O_2$) gases, respectively, using the technique described in [9]. The energy E deposited into a wire was calculated from waveforms of the current, $I(t)$, and voltage, $U(t)$, by the method of substitution of the integral

$$E = \int_{t_0}^{t_n} U(t) I(t) dt \tag{1}$$

by a finite sum. The relative error of energy estimation was $\sigma \leq 13\%$. The amount of overheat of the wire metal was determined, according to [10], from the expression

$$W = \frac{E}{(E_s V)}, \tag{2}$$

where E is the energy deposited into the wire, in J; E_s is the energy of metal sublimation, in J/m^3, and V is the wire volume, in m^3.

The TEM images of nanoparticles were registered by a JEM-2100 transmission electron microscope (JEOL, Japan). The elemental composition and the distribution of elements in the nanoparticles were studied using an X-Max detector combined with the microscope. The average particle diameter (a) was calculated from the equation for the specific surface area

$$S = \frac{6}{\rho a}, \tag{3}$$

where ρ is the specific metal density, in kg/m^3; a is the average particle diameter, in m; and S is the specific surface area of nanoperticles, in m^2/kg.

The aluminum content in nanopowders was determined by the volumetric method. The content of aluminum nitride in Al–AlN was determined by the spectrophotometric method using the Nessler reactant with a Spekol 1300 spectrophotometer (Analytik Jena AG, Germany) from the amount of ammonium deposited as a result of AlN hydrolysis.

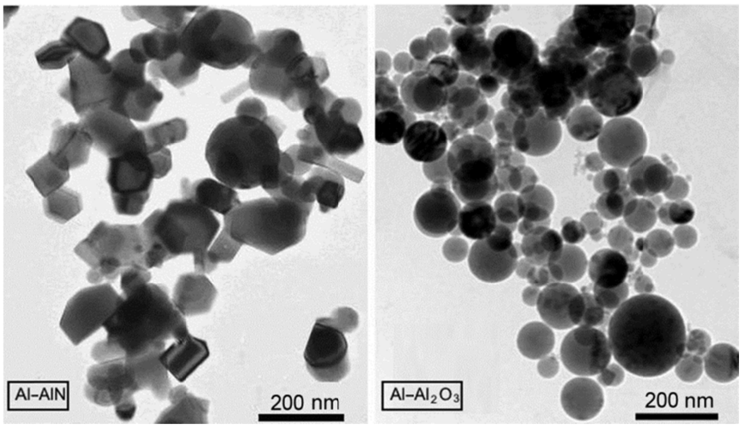

Fig. 1. Characteristic image of nanoparticles synthesized via electric explosion of aluminum wires.

RESULTS AND DISCUSSION

Electric explosion of an aluminum wire was observed for metal overheat $W \geq 0.6$. The amount of overheat W of the wire metal determines the initial temperature of explosive products and the rate of their expansion υ into the surrounding (buffer) gas. With increasing W, the rate υ also increased, since the thermal energy of explosive products will be converted into the kinetic energy of their expansion. The expanding explosive products retain cylindrical symmetry for some time without mixing with the buffer gas; in this case, the density of the substance in the cylinder formed by the explosive products exceeded considerably the buffer gas density [10].

Figure 1 shows the characteristic TEM images of nanoparticles synthesized via explosion of aluminum wires with diameter $d_0 = 0.35$ mm in the N_2 atmosphere and Ar + O_2 gas mixture (with oxygen content of 20 vol.%) under the pressure $P = 10^5$ Pa and $W = 1.5$. An analysis of the TEM images demonstrates that the Al–AlN nanoparticles have faceted forms (Fig. 1), whereas the Al–Al_2O_3 nanoparticles are almost regular spheres.

Dependences of the aluminum oxide and nitride concentrations C on the amount of overheat W are shown in Fig. 2. From the figure it follows that at $W = 0.6$, the aluminum oxide and nitride concentrations in nanopowders are close.

With increasing W the aluminum oxide and nitride concentrations quickly increased up to $W \approx 1.2$. For $W > 1.2$, the Al_2O_3 concentration reached 100 mass%, and the AlN concentration was about 70 mass%. The main growth of the Al_2O_3 and AlN concentrations was observed in the range $W \approx 0.6$–1.2. The oxygen molecule has higher chemical reactivity than the nitrogen molecule. From the analysis performed in [11] it follows that the energy of bond braking in the O_2 molecule is 493 kJ/mol, which is approximately twice less than the dissociation energy of the N_2 molecule (940 kJ/mol). Even at 3000°C the degree of dissociation of nitrogen molecules reached only 0.1%. Therefore, in analogous conditions Al_2O_3 is formed more intensively than AlN.

By analogy with the concentration of chemical compounds, the average size of nanoparticles synthesized in the nitrogen and oxygen atmospheres quickly decreases when the amount of overheat increases in the range $W \approx 0.6$–1.2 (Fig. 2). Further increase in overheat has practically no effect on the nanopowder dispersion.

Thus, overheat of wires has the main influence on the concentration of aluminum chemical compounds and on the average size of nanoparticles in the range $W \approx 0.6$–1.2 with other parameters remaining the same. The formation of aluminum oxide and nitride phases will be determined by the aggregate state of the explosive products. According to [12], the explosive products represent a system of submicron particles distributed through metal vapor. In [13] it was established that there existed a certain radial rate of conductivity loss that depended on the amount of overheat of the metal wire. The resistance of the exploding wire had a maximum at $W = 1.0$ (metal sublimation energy) and decreased

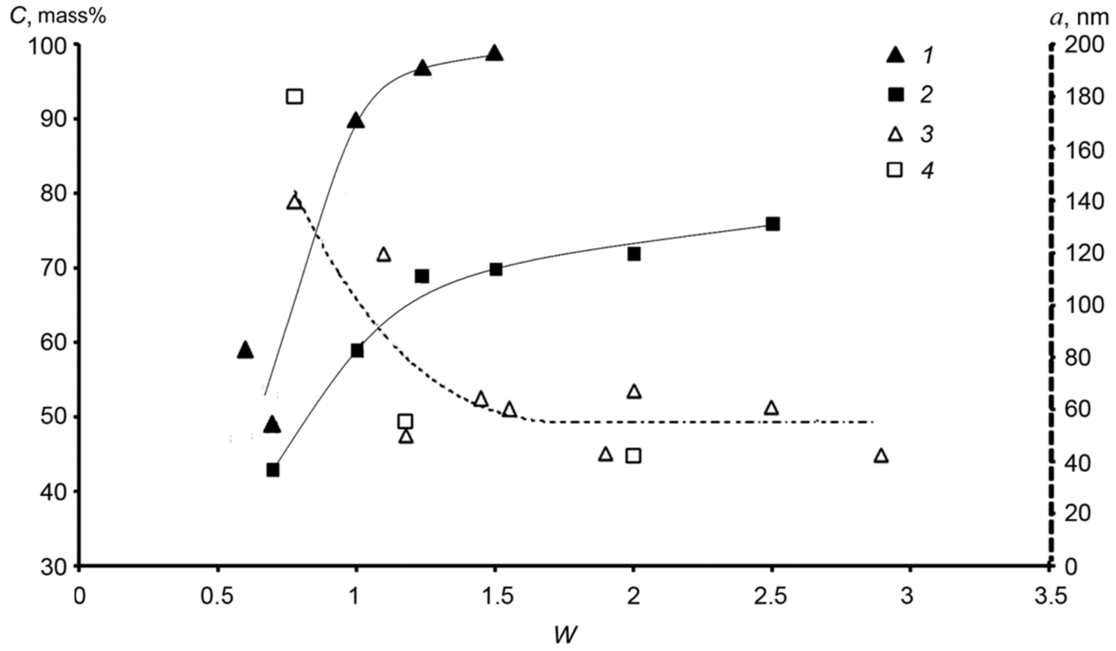

Fig. 2. Dependence of the concentration *C* of aluminum oxide and nitride phases on the amount of overheat *W*. Here curve *1* is for the Al_2O_3 concentration, wire diameter $d_0 = 0.31$ mm, gas mixture Ar + 16 vol.% O_2, and pressure of the gas mixture $P = 10^5$ Pa; curve *2* is for the AlN concentration, wire diameter $d_0 = 0.10–0.31$ mm, and nitrogen pressure $P_N = 10^5$ Pa; curve *3* is for the average size of particles synthesized via explosion of an aluminum wire in the nitrogen atmosphere; and curve *4* is for the average size of particles synthesized via explosion of an aluminum wire in the mixture of argon + oxygen (20 vol.%) gases. In experiments *3* and *4*, $d_0 \approx (0.30–0.38) \cdot 10^{-3}$ m and $P = 10^5$ Pa.

with increasing amount of overheat for $W > 1.0$. The authors explained this fact by ionization of exploding metal vapors that increased with overheat; because of this, the wire resistance decreased.

From [14] it is well known that thermal ionization of metal vapor starts when the phase trajectory of metal reaches the bimodal (the boundary of the region of existence of the two-phase substance). This suggests that, owing to quick energy deposition when the amount of overheat is less than the aluminum sublimation energy ($W < 1.0$), the wire metal is mostly in the condensed state, and the fraction of metal vapor is relatively small. Intensive vapor formation and hence metal vapor ionization occur at $W = 1.0$. This assumption is also confirmed by the data presented in [15] from which it follows that the explosive boiling during EEW starts in the vicinity of the binodal. Hence, the portion of energy exceeding that of metal sublimation ($W > 1.0$) is deposited into the ionized and expanding wire substance and is transformed into the kinetic energy of separating explosive products. Owing to the current running through the ionized vapor, no significant overheating of submicron particles further occurs, and the mass ratio of the condensed and vapor phases remains practically unchanged. Thus, for $W < 1.0$ the energy deposited into the wire is mostly spent on metal heating, and for $W > 1.0$ it is spent on an increase in the expansion rate of the explosive products.

The increase of the expansion rate of the explosive products with increasing *W* has no significant effect on the increase of the mass fraction of aluminum nitride in AlN/Al and sizes of nanoparticles synthesized in the oxygen-containing atmosphere and in nitrogen (see Fig. 2). With increasing pressure (*P*) of N_2 and Ar + O_2 gases, a relatively slight increase in the mass fraction of aluminum nitride and a sharp decrease in the Al_2O_3 concentration are observed in powders (see Fig. 3). With increasing *P* the diffusion rate of the Ar + O_2 mixture and N_2 through the contact surface between the cylinder of expanding explosive products and the buffer gas should increase. As a result, the concentration of chemical compounds must increase. However, in the case of synthesis of Al_2O_3, the reverse effect is observed,

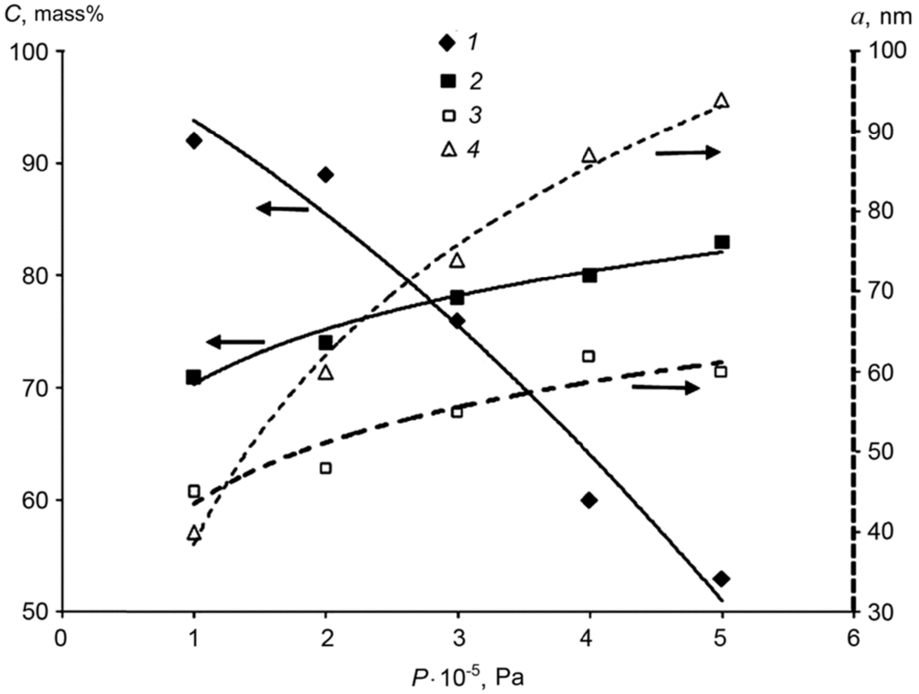

Fig. 3. Dependences of the concentrations *C* of oxide and nitride phases and of the average nanoparticle size *a* on the pressure *P* of the argon – oxygen (12 vol.%) gas mixture and nitrogen. Here curve *1* is for AlN concentration, curve *2* is for Al_2O_3 concentration, curve *3* is for the average size of AlN nanoparticles, and curve *4* is for the average size of the Al_2O_3 nanoparticles. The wire diameter in the experiments was $d_0 = 0.31$ mm and $W = 1.1–1.3$.

namely, an increase in the pressure of the $Ar + O_2$ mixture leads to a noticeable decrease of the mass fraction of aluminum oxide in nanopowders (curve *2* in Fig. 3).

The reaction of aluminum oxidation is limited only by the oxygen delivery to the reaction zone. With increasing *P* the rate of cooling of explosive products increases since their kinetic energy is spent the faster, the higher is the pressure of the buffer gas. Accordingly, aluminum oxidation starts at a smaller area of the contact surface accessible for the chemical reaction and a higher density of the explosive products. As a result, the mass fraction of Al_2O_3 in nanopowders decreases with increasing pressure.

The reaction of interaction of aluminum with nitrogen is limited by the temperature of explosive products. Thermal dissociation of aluminum nitride proceeds at temperatures 2400–2700 K that is lower than the temperature of aluminum boiling (3070 ± 100) K. On the other hand, the energy of aluminum sublimation is 18.8 kJ/mol which is much lower than the dissociation energy of nitrogen molecules (940 kJ/mol). From the foregoing estimates it follows that the process of aluminum nitriding in the gas phase during EEW is improbable.

Thus, the nitrogen interaction with the aluminum vapor via diffusion through the contact surface between the explosive products and the buffer gas is not critical for the formation of aluminum nitride. The formation of AlN in the condensed phase via the nitrogen diffusion to aluminum nanoparticles after their formation in the process of mixing of explosive products with nitrogen is more probable.

The increase in *P* leads to an advancing growth of the average size of nanoparticle synthesized in the oxygen-containing atmosphere relative to the size of the nanoparticles synthesized in nitrogen (Fig. 3). It is probable that the energy liberated during aluminum oxidation increases the cooling time of the dispersed system and hence the formation time of the nanoparticles containing Al_2O_3. In [3] it was emphasized that in the process of oxidation the aluminum particles evaporate at the expense of the oxidation heat, and in the process of repeated condensation, aluminum oxide is

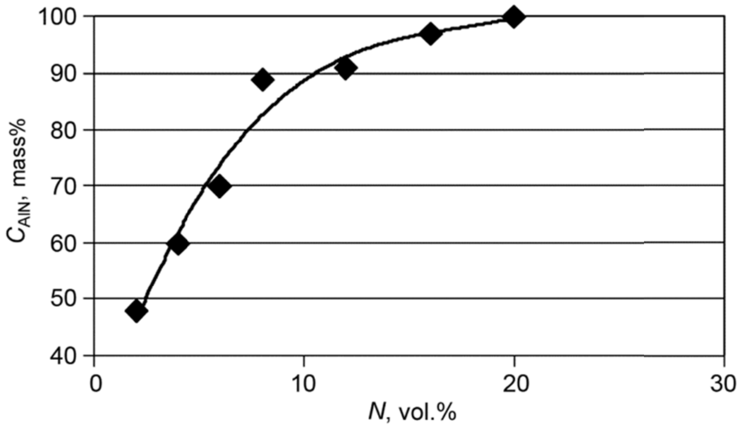

Fig. 4. Mass fraction of Al_2O_3 depending on the oxygen content in the argon atmosphere for the pressure of the gas mixture $P = 10^5$ Pa, the wire diameter $d_0 = 0.31 \cdot 10^{-3}$ m, and $W = 1.2–1.26$.

formed. Thus the nanoparticles can be in the liquid state which is testified by their spherical shape (see Fig. 1) and facilitates the process of their association.

Since Al_2O_3 is formed in the course of the reaction in the gas phase with uncontrollable aluminum evaporation, the formation of aluminum oxide layers of a predetermined thickness on the nanoparticles is unlikely. In addition, as can be seen from Fig. 4, even for relatively low oxygen content in the mixture of gases (nearby 2 vol.%), the mass fraction of aluminum oxide exceeds 45 mass%. In our opinion, such considerable content of Al_2O_3 will make it impossible for the aluminum core of the nanoparticles to enter into the reaction with water.

It is obvious that controllable oxidation of nanoparticles after their synthesis in an inert atmosphere is a more perspective method for obtaining thin Al_2O_3 layers on the surface of the aluminum core. The formation of AlN can proceed via diffusion of molecular nitrogen into the nanoparticles in the condensed phase. This conclusion is in agreement with already known experimental facts. The reaction of finely dispersed aluminum powder with nitrogen is possible already at temperatures 803–898 K, that is, at temperatures lower than the melting temperature of the metal.

When the aluminum nanoparticles come in contact with nitrogen, solid aluminum nitride is nucleated on the nanoparticle surfaces. The number of aluminum nitride nuclei increases due to fast growth of already existing nuclei and relatively slow formation of new nuclei. Because of the predominant growth of originally formed nuclei, the nanoparticles start to acquire irregular shape (see Fig. 1). The growing nuclei merge forming the continuous layer of aluminum nitride. In this case, along with AlN nanoparticles comprising nitrogen and aluminum approximately in stoichiometric ratio (see Fig. 5 and Table 1), particles with the central part enriched with aluminum (indicated by point *3* in Fig. 5) are detected in the nanopowders.

The AlN nanoparticles basically have smaller sizes in comparison with nanoparticles of other morphologies. Such nanoparticles can be formed during nitrogen interaction with the aluminum particles having the least sizes thereby leading to their complete nitriding. The largest particles have the morphology shown in Fig. 5 with the central part enriched with aluminum. The similar structure can be formed when the nitrogen diffusion into the metal core is hindered by the continuous aluminum nitride layer formed on the aluminum particle surface.

Particles having irregular core that probably consists of AlN are also presented (Fig. 5). The layer of practically pure aluminum is localized on the core surface (points *6* and *7* in Fig. 5). Along with the condensed phase, the metal vapor is present in the explosive products. When the nitrogen content decreases in the regions of forming AlN particles, the aluminum vapor will be condensed on the aluminum nitride nanoparticle surface. This leads to the formation of nanoparticles with the above-indicated morphology. Despite the complex morphology of nanoparticles synthesized via EEW in nitrogen, the conditions of the process at which the maximum AlN concentration is reached in nanopowders are quite obvious: $W > 1.2$ and $P \geq 0.5$ MPa.

TABLE 1. Content of Elements at the Points of Analysis

Point of analysis	Al, at.%	N, at.%	O, at.%
1	57.25	41.17	1.58
2	70.13	25.10	4.77
3	83.92	13.09	2.99
4	72.92	21.72	5.36
5	78.31	13.46	8.23
6	82.95	1.64	15.41
7	73.99	19.37	6.64
8	60.05	33.89	6.06

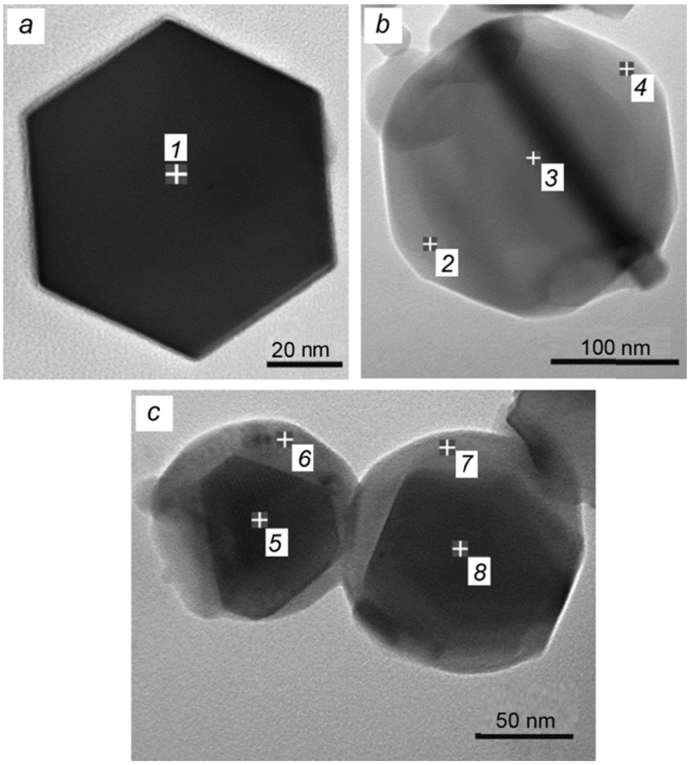

Fig. 5. Images of AlN nanoparticles (*a*) with the central part enriched with aluminum (*b*) and with the coating enriched with aluminum (*c*).

CONCLUSIONS

1. During expansion of the wire substance into the Ar + O_2 gas mixture, the oxidation occurs on the contact surface between the explosive products and the gas. Nitriding reaction proceeds in the condensed phase via to nitrogen diffusion into the aluminum nanoparticles after their formation during mixing of the explosive products with nitrogen.

2. The mass fraction of aluminum oxide in nanoparticles synthesized via EEW in the mixture of Ar and O_2 gases can be regulated in the range of overheat $0.6 < W < 1.2$, pressure of gas mixtures 0.1 MPa $< P <$ 0.5 MPa, and oxygen concentration 2 vol.% $< N <$ 20 vol.%. In this case, the minimal content of aluminum oxide obtained in the

experiments exceeded 45 mass%. For this reason, it is difficult to obtain thin aluminum oxide layers on the surface of aluminum nanoparticles synthesized via EEW because of high reactivity of aluminum with oxygen.

3. The mass fraction of aluminum nitride in nanoparticles synthesized via EEW in nitrogen can be regulated in the range of overheat $0.6 < W < 1.2$ and pressure of gas mixture 0.1 MPa $< P < 0.5$ MPa. The maximal content of aluminum nitride in the nanopowders will be observed for metal overheat $W > 1.2$ and nitrogen pressure $P \geq 0.5$ MPa.

4. The average size of nanoparticles synthesized by electric explosion of an aluminum wire in the $Ar + O_2$ gas mixture and in nitrogen decreased with increasing amount of metal overheat in the range $0.6 < W < 1.2$. With further increase of overheat $W > 1.2$, the nanoparticle sizes remain unchanged.

5. From the data obtained it follows that for overheat $W < 1.2$ the energy deposited into the wire is spent basically on heating of the condensed phase, and for $W > 1.2$, it is spent on the increase in the expansion rate of the explosive products.

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