FORMATION MECHANISM OF THE METALLIC NANOSTRUCTURES USING PULSED AXIAL ELECTROTHERMAL PLASMA ACCELERATOR

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Paper is devoted of the formation mechanism of metal the nanoparticles in the development of high-current pulsed electric discharge in a limited volume at atmospheric pressure. The original design of the axial electrothermal plasma accelerator was used to create the discharge operating in the gas-dynamic mode. The analysis of chemical composition and dimensions of the formed particles was carried out. It is established that formation of nanoparticles caused solely through the mechanism of nonequilibrium condensation of supersaturated vapor.

PACS: 52.77. - j

INTRODUCTION

Nowadays there exist various methods of formation of dielectric, semi-conductor and metallic nanoparticles and nanostructures [1,2]. The well-known technologies are divided into two basic groups: "top-down" and "bottom-up". The first group is based on receiving nanoparticles from macro-objects, for instance, by mechanical crushing of a solid body, selective removal of the material, previously inserted upon the substrate layer or three-dimensional metal treatment by means of ionic beams. The second group is based on synthesizing of nanoparticles by means of merging of separate atoms and is carried out at chemical reactions inside a solid body, or chemical reactions in nanodimensional scale, based on the principal of colloid chemistry, on the reverse micelle method.

The simplest and most promising for practical application is the gas-phase method for the synthesis of nanoparticles (bottom-up), at which metal, alloy or semi-conductor is evaporated both in vacuum and in the atmosphere of inert gas and low pressure with subsequent steam condensation. This is the simplest method of obtaining nanocrystal powders. For example, condensation of aluminum vapours in *Ar* and *He* at various gas pressure made it possible to obtain particles 100 to 20 nm in dimension. Besides of simplicity the advantage of the method is to obtain from the gas-phase isolated nanoparticles and their clusters.

Devices which use the principle of evaporation and condensation, differ by the method of introduction of the material to be evaporated, the method of supply energy for evaporation, the working environment etc. Evapouration and condensation can take place in vacuum, inside motionless inert gas, in gas flow, including plasma jet. There are techniques in which the condensat chamber coaxially comes two jets – steam gas mixture is fed along the axis, and on the periphery of the jet enters a cold inert gas. As a result of the turbulent mixing of the metal vapor temperature drops sharply and there is a rapid condensation. Evaporation of the metal can occur out of the crucible by the ion beam or electron laser beam. Metal may enroll in zone heating and evaporation, for example, in the form of wire.

As can be seen, all these installations are quite complex, and the produced particles are characterized by significant variation in size and parameters of the synthesized materials.

In [3] an original design of an impulse axial electrothermal plasma accelerator is described, which works in gas-dynamic mode. Its principle of work is based upon development of a high-current impulse electric discharge inside limited volume at atmospheric pressure. Given system allows forming high enthalpy gas-plasma flow. In [4] a similar device was used as reactor ceramic nanomaterials. From our point of view this accelerator can be used not only for obtaining ceramic nanomaterials, but also for formation of metallic nanoparticles. It should be noted here that a high-current pulsed electric discharge is used as a working environment in nanomaterials reactors quite often [5, 6]. It is in during of high-current pulsed discharges were received high energy parameters of supersaturated vapor. It should be noted that in the above devices synthesized nanomaterials scatter, in practice, by the solid angle of 4π. But an pulsed axial electrothermal plasma accelerator permits to form a directed substance flow, which significantly increases its manufacturabilityas when using in nanophysics and in plasma technology.

However, when the pulse energy release at the surface of metals and alloys, exceeding the level of ablation remains unclear mechanism of nanostructure formation: formation of nanoparticles is due to the condensation of supersaturated vapor evaporating substance or by spraying droplets of a liquid metal? In some works, this process is associated with the formation of ectons on the cathode's surface in electrical discharges with subsequent spraying of metal droplets [7]. In other works has been suggested that the formation of nanoparticles in these conditions is due to the non-equilibrium condensation of the metal vapor [8]. This equally applies to the pulse electrothermal axial plasma accelerators, as the reactor metallic nanoparticles. In this connection purpose of the present work is to study formation mechanism of metallic nanoparticles, synthesized with application of an pulsed axial electrothermal plasma accelerator (PA).

1. AN EXPERIMENTAL DEVICE

This work was preceded by the results published in [9] in which the nanoparticles were obtained during the development of a pulsed high-voltage vacuum dis-

charge, accompanied by the emergence of micro-explosions on the surface of the cathode and the formation ectons [7, 10].

In these experiments were investigated receipts of nanoscale materials using a pulsed high-current discharge at atmospheric pressure with adiabatically expanding super-sonic gas stream, to study the chemical composition and dimensions of the synthesized particles.

For the experiments used PA, its diagram is shown in Fig. 1. The housing 1 was made of a thick-walled rigid paper – bakelite tube 40 cm in length. The internal diameter was – 8 mm, the wall's thickness being 1 cm. The edges of the dielectric shell were pressed with metal shells 3 and 4. A changeable rod electrode 2 6 mm in diameter is fixed to the shell 3, acting as a cathode. One end of this electrode is inserted into the internal channel inside the shell, the other one protrude outside. A metal shell 4 with an orifice 5 acts as an anode, its diameter being 6 mm. The distance between the cathode and the circular anode was regulated within the level 8 to 15 cm. Anode 4 was grounded, and voltage from capacitive energy storage was applied to the rod cathode. The material of the rod cathode used in the work: bronze, Fe, Al, Cu, Pb. Operating pressure – atmospheric, working gas-air.

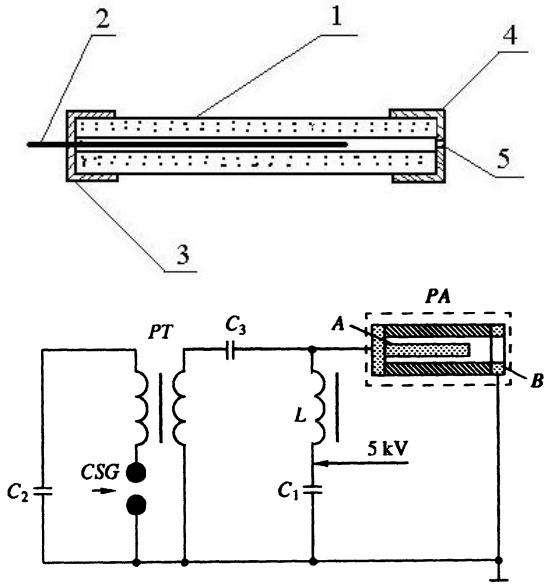

Fig. 1. Axial electrothermal plasma accelerator – atop, and to the down its electrical circuit

Electrical block diagram of the plasma accelerator, consisting of a capacitive storage and starting circuits is shown o in the bottom part of Fig. 1. Capacitor's value $C1 = (1.5…3.0)\cdot 10^{-3} f$, working voltage up to 5 kV and the maximum storage energy was changed within the values equal to (18.75…37) kJ. Triggered scheme includes elements C1 and L. Detailed description of the the element base of the scheme and obtained the current-voltage characteristics is given in [3].

A high-current pulsed arc with high pressure discharge was initiated between the cathode and the anode, restricted by a narrow dielectric channel. The charge duration was 1.4 ms, the maximal current reached 4 kA. The working substance, in this case, is supplied into the charge's channel by means of intensive evapouration of electrodes and the wall's substance of dielectric chamber. As the result pressure inside the channel is shortly raised to (100…150) atm. An impulse injection of a dense gas-plasma clot through the circular anode into the surroundings takes place. The working mode of this plasma accelerator is gas-dynamic. Plasma parameters were estimated: density and temperature about 10^{16} cm^{-3} and (1…2) eV, correspondingly. Discharge accompanied by light intensity and sound effect. Fig. 2 presents a photograph (a violet filter was used) of a plasma clot. Length of the light formation reached 0.8 m.

Fig. 2. A photograph of plasma clot

Gas-plasma clot's flow through the circular anode into the surroundings happens in adiabatic mode at supersonic velocity, this is verified by formation of "barrels", which could be seen in the photograph and by direct measurement of velocity with application of optical sensors. Expiration of gas-plasma clot through the annular anode into the environment is in the adiabatic regime at a supersonic speed, as evidenced by the formation of "barrels" that are visible in the photograph, and the direct measurement of the velocity using optical sensors.

2. EXPERIMENTAL RESULTS AND DISCUSSION

For collection and subsequent analysis of micro particles glass plates were used, their sizes being (3×3) cm, they were installed at the distance (6…8) cm from the circular anode outside PA. The particles were collected upon a glass substrate per one impulse. Their sizes were investigated by means of a scanning electronic microscope ISM-6390LV (manufactured by IEOL company, Japan), the accelerating voltage being 10 kV and the maximum resolution ~ 20 nm and more. Fig. 3 presents the photographs of erosion products the iron and aluminum cathodes. The number of particles various sizes in a single photo is 300…500 pieces.

As it follows from the photographs, supplied on the substrates both particles of nanometer range and the particles in the form of large drops of micrometer range can be seen. It is important to note that this method of forming a gas-plasma clot it may contain the atoms and molecules of the wall material, the electrodes and the air, which may lead to the formation of oxides, nitrides, and hydrocarbon groups. Moreover, inside the combustion products of a heavy current arc are presence and ejection of drops fraction of electrodes materials can occur. Hence, it is of interest to investigate the chemical composition of the synthesized particles and the mechanism of their formation.

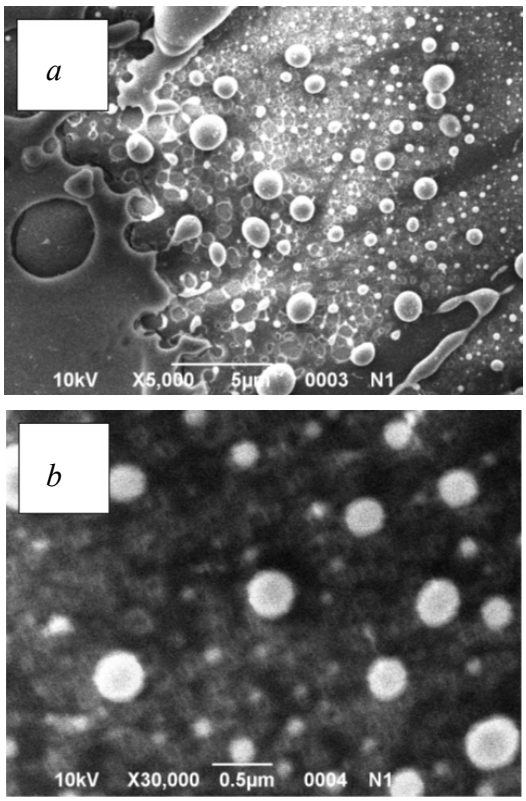

Fig. 3. Pictures of nanoparticles. Scales are indicate on each picture: a) iron (magnification 5 000, scale – 5 μм); b) aluminum (magnification 30 000, scale – 0.5 μм)

X-ray fluorescent analysis was used with this purpose in this work. The investigation was performed on Thermosinetific OXAS (Switzerland) instrument. For this analysis was carried out X-ray spectra of nanoparticles on glass substrates and the spectra of the electrode material, resulting in what can be compared to the elemental composition of the starting material with the composition of the synthesized nanostructures.

The Table contains the results of such comparative analysis for a bronze cathode. It should be noted that it was the cathode, which underwent the biggest erosion in the charge. In the table in the left part (printed in bold type) elements composition of nanoparticles on the glass can be seen, in the right part there is the chemical composition of the bronze cathode. As it can seen in the table the elements like *Si, Ca, Na, Mg* et al., which are present in the left list and are missing in the right, for mass composition one attribute to about ≈ 81 %, reflecting the chemical composition of glass. For copper mass share, which is nearly 82% in bronze, in nanoparticles its share is only 5.56%.

If we deduce the mass share of the aforementioned elements, and the remaining ≈ 19 %, i.e. the mass share of nanoparticles multiply by 5 (in order to get ≈100% as the result), then we'll get ≈ 27.8% for copper. This value is substantially lower than copper content in bronze. For aluminum, the situation is reversed in light of the above, its share in the nanoparticles is increased to ≈ 31.5%, and in bronze, its share was 12.17%.

A similar discrepancy between the elemental composition in nanoparticles and in bronze is also observed for the other elements. Thus, the percentage of the same elements for the cathode and for nanoparticles, synthesized on the substrates differs substantially. It is important to note here that a number of elements, peculiar to the original bronze cathode was missing in the synthesized nanoparticles. Such elements, like *Ge, Hg, Ta, Zn, W* were not found in nanoparticles. The same regularity is typical for other alloys, used for cathode, particularly for iron and aluminum.

Elements composition of nanoparticles and cathode's material for bronze

El	m/m%	StdErr%		El	m/m%	StdErr%
Si	55.19	0.25		**Cu**	82.02000	0.2000
Ca	11.29	0.16		**Al**	12.17000	0.2000
Na	10.64	0.15		**Mn**	2.39000	0.0800
Al	6.30	0.12		**S**	0.60300	0.0380
Cu	5.56	0.11		**Cl**	0.51200	0.0410
Fe	4.27	0.10		**Si**	0.47100	0.0460
Mg	3.34	0.09		**W**	0.37300	0.0220
K	1.32	0.06		**Fe**	0.34600	0.0170
Ti	0.547	0.027		**Ni**	0.24500	0.0120
Px	0.488	0.024		**Au**	0.22100	0.0270
Sx	0.332	0.017		**Zn**	0.17600	0.0090
Mn	0.307	0.015		**Ta**	0.15000	0.0700
Ni	0.167	0.008		**Ca**	0.13900	0.0120
Cl	0.0997	0.0087		**Hg**	0.09600	0.0190
Cr	0.0947	0.0047		**Cr**	0.05350	0.0055
Zr	0.0164	0.0029		**K**	0.02280	0.0083
Ar	0.0147	0.0061		**Ge**	0.01390	0.0062
Rb	0.0125	0.0024		**–**	–	–
Sr	0.0058	0.0026		**–**	–	–
	99.9948	–		**–**	100.0022	–

This means that the formation of nanostructures in the conditions of this experiment is not due to the result of the "splashing" of metal droplets but exclusively because of the non-equilibrium condensation of supersaturated vapor metals. This mechanism of nanoparticles formation is similar to condensation of metallic vapours at adiabatically expanding super-sonic stream in Laval's nozzle, when as the result of quick expansion a high temperature gradient is formed and almost immediate vapour condensation occurs [1]. A similar situation occurs in our case – the supersonic flow of gas and its rapid cooling and the rapidly drop in pressure in the discharge channel from hundred atmospheres up to several Torr [11].

MAIN CONCLUSIONS

1. The paper demonstrated the possibility of producing nanoscale metal particles in the development of high-current pulsed arc discharge in a limited narrow dielectric channel at atmospheric pressure. We used the axial electrothermal plasma accelerator, working in a gas-dynamic mode. The indisputable advantage of this method is the absence of a vacuum system, which significantly simplifies the experimental technique.

2. On the basis of X-ray fluorescence analysis showed that the synthesis of nanoparticles in the experimental conditions occurs exclusively by homogeneous condensation of supersaturated vapor cathode material. This mechanism leads to the formation of particles as nanometer and micrometer range.

3. There is reason to believe that such a mechanism is predominant in the synthesis of nanostructures using pulsed concentrated energy flows and the role of dispersal and fragmentation of the drop fraction of the liquid metal cathode to the individual nanoparticles is found to be insignificant. That is the dominant mechanism for the "bottom up".

4. The design of the plasma accelerator used in the experiments allows to obtain nanoparticles of all metals and alloys. Performance of nanomaterials is ~ 100 kJ/g.

REFERENCES

1. V.V. Klimov. *Nanoplazmonika.* Moscow: "Fizmatlit", 2009, 480 p. (in Russian).
2. A.I. Gusev. *Nanomaterials, nanostructures, nanotehnologii*. Moscow: "Fizmatlit", 2009, p. 416.
3. Yu.E. Kolyada, V.I. Fedun, I.N. Onishchenko, E.A. Kornilov. The use of a magnetic switch for commutation of high-current pulse circuits // *Instruments and Experimental Techniques*. 2001, v. 44, № 2, p. 213-214.
4. United States Patent № 6472632, October 29, 2002. D.R. Peterson, D.E. Wilson. Method and apparatus for direct electrothermal-physical conversion of ceramic into nanopowder.
5. V.S. Koidan, E.E. Barkalov, M.N. Kazeev, V.F. Kozlov, Y.S. Tolstov. The formation of nanostructures with erozii electrodes in pulsed discharge // *4th All-Russian Conference on Nanomaterials. Moscow. 01-04 March 2011. Book.-M.: Institute of Metallurgy, Russian Academy of Sciences*. 2011, p. 88.
6. United States Patent № 6777639, August 17, 2004. K.A. Schroder, D.K. Jackson. Radial Pulsed Arc Discharge Gun For Synthesizing Nanopowders.
7. G.A. Mesjats. Ecton-electron avalanche from metal // *Uspehi Physicheskih Nauk.* 1995, v. 165, № 6, p. 601-626 (in Russian).
8. E.L. Fenko. *Generation of ultradisperse particles during irradiation of a metal target with a powerful electron beam.* Avtoreferat diss. Candidate Physics and Mathematics Sciences, Ekaterinburg, 2010.
9. Yu.E. Kolyada, O.N. Bulaunchuk, V.I. Fedun, I.N. Onishchenko. Aerosol microparticles and emission characteristics of the pulsed high – current vacuum diode in a microsecond range // *Proceedings of the 19th International Symposium on Discharges and Electrical Insulation in Vacuum. – Xi'an, China.* September 18-22, 2000, v. 1, p. 68-71.
10. S.A. Popov, D.I. Proskurovsky, A.V. Batrakov. Regularities of formation droplets an explosive liquid metal cathode // *Izvestija vuzov. Physics*. 1999, № 3, p. 105-108 (in Russian).
11. Yu.E. Kolyada. Formation of high-current electron pulse beams outside the vacuum conditions // *Technical Physics Letters*. 2000, v. 26, № 16, p. 52-56.

Article received 15.03.2013

МЕХАНИЗМ ФОРМИРОВАНИЯ МЕТАЛЛИЧЕСКИХ НАНОСТРУКТУР С ИСПОЛЬЗОВАНИЕМ ИМПУЛЬСНОГО ЭЛЕКТРОТЕРМИЧЕСКОГО ПЛАЗМЕННОГО УСКОРИТЕЛЯ

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Исследуется механизм формирования металлических наночастиц при развитии сильноточного импульсного электрического разряда в ограниченном объёме при атмосферном давлении. Для создания разряда использовалась оригинальная конструкция электротермического плазменного аксиального ускорителя, работающего в газодинамическом режиме. Проведён анализ химического состава и размеров синтезированных частиц. Установлено, что формирование наночастиц обусловлено исключительно за счёт механизма неравновесной конденсации пересыщенного пара.

МЕХАНІЗМ ФОРМУВАННЯ МЕТАЛЕВИХ НАНОСТРУКТУР З ВИКОРИСТАННЯМ ІМПУЛЬСНОГО ЕЛЕКТРОТЕРМІЧНОГО ПЛАЗМОВОГО ПРИСКОРЮВАЧА

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Досліджується механізм формування металевих наночастинок при розвитку потужнострумового імпульсного електричного розряду в обмеженому обсязі при атмосферному тиску. Для створення розряду використовувалася оригінальна конструкція електротермічного плазмового аксіального прискорювача, працюючого у газодинамічному режимі. Проведено аналіз хімічного складу і розмірів синтезованих частинок. Встановлено, що формування наночастинок обумовлено виключно за рахунок механізму нерівноважної конденсації пересиченого пару.