

# **Nanostructure Ag and Cu coatings on powder materials**

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## **1. Introduction**

Functional coatings are an integral part of practically all kinds of products made by man, for instance, the poisonous coating on the tip of an arrow, the protective coating of a cosmonaut descent capsule with the cosmonaut of the space vehicle or a soluble shell of a drug. Depending on coating purpose, various materials, structures and processing methods are applied. Among the numerous modern chemical, electrochemical and physical methods and technologies to produce coatings, physical processes of evaporation and condensation of various materials in vacuum are certainly noteworthy. Condensation of the vapors of various materials in vacuum provides a unique complex of methods to produce both new materials and coatings with micro- and nanosized structure.

In the middle of the twentieth century, intensive development of vacuum technologies for thin film deposition ( $< 1 \mu\text{m}$ ) took place, from anti reflecting or reflecting optical coatings to an independent class of semiconductor thin-film materials which formed the basis of modern microelectronics and computer technologies. Synthesis of solid-state thin-film structures by controlled atom packaging from the vapor allowed creation of miniature devices with dimensions and specific characteristics, which seemed fantastic in recent past.

In the vapor phase materials “do not know” the laws of solubility. Therefore, by performing simultaneous or successive evaporation and condensation of several materials, it is possible to produce such combinations (compositions) of components and structures, which are difficult or impossible to create by other methods. Simultaneously with development of thin film technologies investigations of “thick films” and coatings of thicknesses from several micrometers up to several millimeters were performed<sup>1,2</sup>.

High-speed evaporation of initial inorganic materials (metals, alloys, and ceramics) is performed by the accelerated electron flow generated by an electron beam gun. The electron beam is one of the most effective heat sources. The main fraction of the kinetic energy of electrons at collision with the heated surface is transformed into thermal energy in a thin surface layer of 1 – 2 mm thickness. Therefore heating by the electron beam the

heat source is in the heated field proper, and ensures maximum completeness of conversion of electric energy into thermal energy. This permits a high level of control of the heating and evaporation processes. To date considerable technological experience has been accumulated with producing inorganic coatings with micro- and nanosized structure by electron beam physical evaporation and deposition i.e. EB-PVD<sup>3,4</sup>.

In today's virtual list of objects which require functional coatings, are powders and granules of inorganic materials (metals, alloys, ceramics) and organic and polymer materials. Examples of nanostructured Ag and Cu coatings produced by EB-PVD on NaCl, Al<sub>2</sub>O<sub>3</sub> and some polymer powders, including medicinal substances and drugs are described herein..

## 2. Substrate materials and methods of investigation of produced coatings

Characteristic examples of inorganic and organic substrate powder materials and their size selected for Ag/Cu nanoparticle deposition investigations are described in Table 1.

Table 1

#	Material	Shape and dimensions of initial granules and powders, mm
1	Sodium chloride (NaCl)	dia. 0.4
2	Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	dia. 0.1
3	Polyethylene (granules)	dia. 3.0
4	Polyvinylpyrrolidone (PVP)	dia. 0.08
5	Metronidazole	0.6×0.5×0.5

To determine the shape and size distribution of Ag metal nanoparticles surface studies were performed in scanning electron microscope (SEM), Tescan Vega 3M. Prior to structure investigations, the nanoparticle composite samples after vacuum drying were fastened to a steel substrate by current-conducting graphite-containing strip to establish electric contact of the studied granule with the substrate. Obtained data were presented in the form of microstructure photographs. Image processing was conducted by determination of dimensions of each particle, calculation of their total number and plotting histograms of size distribution. Statistical processing of obtained data and histogram plotting were performed and the number of analyzed metal particles was not less than 800 pts for each sample. A common feature of nanoparticles in a liquid matrix produced by any method is their proneness to coalesce into aggregates, so that it is

necessary to take into account not only the dimension of individual nanoparticles, but also dimension of their aggregations. To determine the actual dimensions and structural stability, nanoparticle size distribution in a colloidal system was measured by the method of laser correlation spectroscopy. For this purpose a water solution was prepared containing 3% PVP with discrete silver coating deposited onto it. Measurements were conducted in laser correlation spectrometer, “Zeta Size -3” (Malvern, Great Britain). At the same time, this solution was also studied using transmission electron microscopy (TEM) by examining the remaining nanoparticles supported on a thin carbon film after complete drying in a HITACHI H-800 microscope at accelerating voltage of 100 kV.

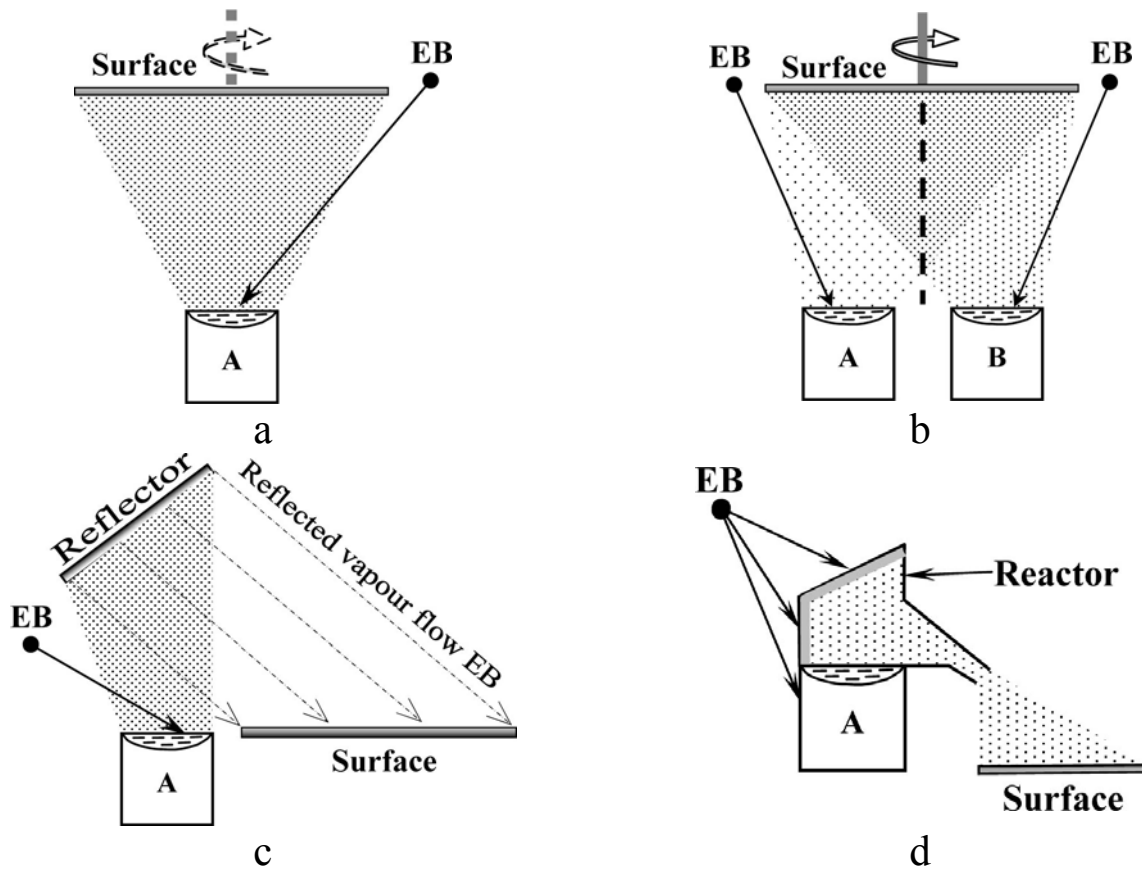
### **3. Technological procedures of electron beam evaporation and coating deposition**

Considering the technological variants of physical processes of evaporation and condensation it should be noted that EB-PVD is conducted in vacuum and is practically not accompanied by harmful vapor or gas evolution into the environment. The technological procedure of evaporation and condensation, as well as evaporator design, is selected in keeping with the problem to be solved.

Fig. 1 gives schematics of some of these processes. Fig. 1a shows simple evaporation by the electron beam (EB) and condensation of the vapor phase on a flat substrate which is stationary or rotating around a vertical axis. Evaporation of material A is performed from a copper water-cooled crucible (cylinder), where evaporation material in the form of an ingot or rod is placed. Liquid pool surface level is kept constant by the mechanism of vertical displacement of the ingot. In production electron beam unit with crucible diameters of 70 mm the following maximum rate of ingot evaporation are achieved: iron – 3.0 Kg/h; nickel alloy -1.5 kg/h; graphite – 1.0 kg/h;  $\text{ZrO}_2$  – 0.8 kg/h. Rate of condensation of the vapor flow on a flat stationary surface located above the pool surface at 300mm distance can reach 30 – 50  $\mu\text{m}/\text{min}$  for metals and alloys and 15 - 20  $\mu\text{m}/\text{min}$  for ceramics (oxides, carbides, borides).

Fig. 1b shows the schematic of simultaneous electron beam evaporation of materials A and B from two independent sources and condensation of a mixed vapor flow on the stationary or rotating substrate. In the presence of a partition between the crucibles shown by a dotted line, the condensate composition and structure will be laminated. Layer

thicknesses are readily regulated by variation of the speed of vertical shaft rotation and rate of evaporation of materials A and B.



*Fig. 1 Technological variants of electron beam evaporation and deposition of coatings.*

Fig. 1c shows the schematic of evaporation with subsequent reflection of the vapor flow from a heated surface (reflector), with the purpose of changing its direction in space, in particular, for vapor flow condensation on the horizontal surface, as shown. Depending on re-evaporated material, the reflector with a polished surface is made from tungsten, high-temperature ceramic or graphite and heated by the electron beam to temperatures of 0.75 – 0.80 of melting temperature (K) of the re-evaporated material. Fig. 1d shows the schematic of evaporation from a graphite enclosed reactor and formation of a directed atomic-molecular flow for relatively low-melting inorganic materials ( $T_m \text{ } ^\circ\text{C} < 1200 \text{ } ^\circ\text{C}$ ) and organic materials, in particular, when controlled pyrolysis is required.

It should be noted that these are basic schematics and in actual embodiments they may have some additions, namely a device for vapor flow ionization, for bleeding reactive gases into the chamber, viewing systems, etc.

Deposition of nanosized coatings on granules and powders is performed using the technological schematics shown in Fig. 1c and 1d. In these experiments the granules or powders were placed into flat copper water-cooled crucibles of 100 – 150 mm diameter and 15 – 20 mm height. Mechanical devices were used to perform their effective mixing with simultaneous “irradiation” by the vapor flow. Temperature of granules and powders during coating deposition was in the range of 30 – 50 C. Depending on the requirements made of coatings; exposure time is in the range of 10 minutes.

Coating formation starts with appearance of nuclei and is completed by formation of a continuous film of required thickness and structure. Theoretical and experimental investigations of these processes have been systematized in many monographs, for instance <sup>5-7</sup>.

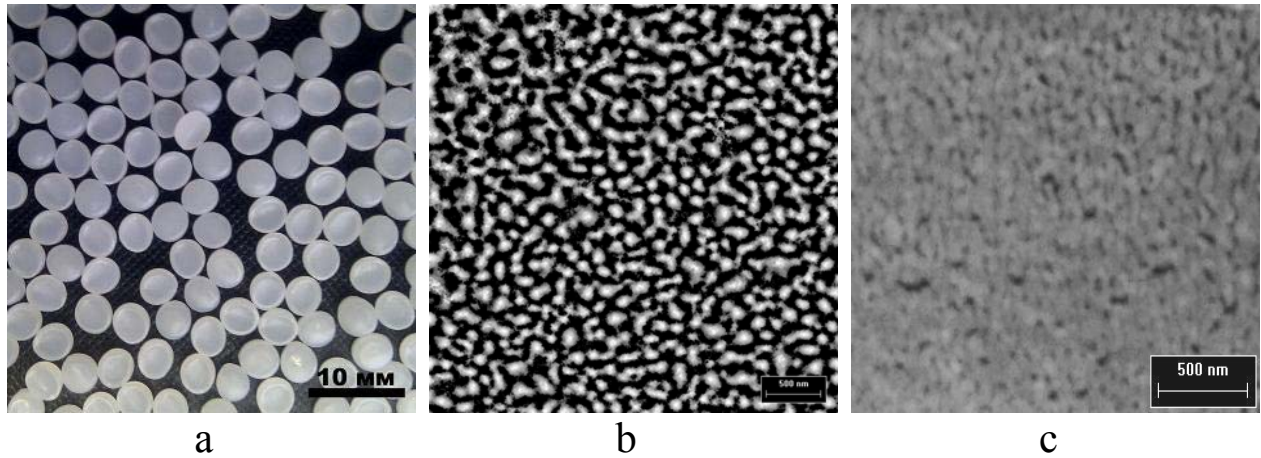
It can be schematically described as follows. Flying atoms or molecules of the vapor flow, when colliding with the condensation surface, are absorbed by it, and moving by diffusion mechanism over the surface, they meet their neighbors to form three-dimensional nuclei. Nuclei are growing quickly, forming characteristic islets. Their shape depends on the value of surface energy and condensation conditions: substrate temperature, vapor flow intensity, etc.

As the islets grow, the distance between them decreases. At the points of meeting of neighboring islets their coalescence takes place, resulting in formation of a ramified network of channels, unfilled with the condensed substance. Further on the channels are gradually overgrown, and turn into isolated pores of various shape. The process of their overgrowing is very slow. The final stage is formation of a continuous film. It should be noted that after the coated item has been removed from the vacuum chamber, at contact with the atmosphere at room temperature oxygen adsorption takes place on the surface of metal nanoparticles with formation of a thin film of oxide (hydroxide).

As an illustration, Fig. 2 shows the islet and practically continuous silver film on polyethylene granules. The coating was produced with an evaporator, the diagram of which is shown in Fig. 1d. Evaporator material is graphite.

Such granules with discrete metal nanocoatings can be deformed by subsequent thermo mechanical treatment (extrusion) into “polymer-metal” composites in the form of fibers, film or shaped item with a high level of respective properties: mechanical, electric, magnetic, bactericidal, etc.

The thickness of continuous metal film,  $h$ , and size of a discrete particle,  $d$ , in the coating can be analyzed, knowing the average size of the



*Fig. 2 Ag coating on polyethylene granules. a) general view of the granules; b) islet structure of silver on the granule surface; c) silver film on the granule surface.*

granule or powder particle,  $D$ , and weight of condensate,  $P$ , deposited in one technological cycle on the surface of granules or powder in a crucible of specified dimensions.

$$P_1 = K \times P_0,$$

where  $P_0$ , is the evaporated metal weight, and  $K$ , is the evaporator efficiency. For instance, for an evaporator of technological variant 1d, depending on the structure, coefficient  $K$  can be varied within the range of 0.15 – 0.80.

As is known, specific surface of powders  $S$ , with average size  $D$ , is equal to:

$$S = 6 \frac{f}{D} \quad \text{eq 1}$$

where  $f$ , is the volume fraction of powder.

Therefore, the total weight of thin coatings of material with specific weight  $\rho$  and thickness  $h$ , deposited on each structural unit, will be equal to:

$$P_1 = S \cdot \rho \cdot h = 6 \cdot \frac{f \cdot \rho \cdot h}{D} \quad \text{eq 2}$$

and thickness,  $h$ , is equal to

$$h = \frac{P_1 \cdot D}{6 \cdot f \cdot \rho} \quad \text{eq 3}$$

As was noted earlier, an “islet” structure forms first. Therefore, at this stage we should consider actual surface  $S_1$  taken up by the particles, i.e.

$$S_1 = n \cdot S, \text{ where } n < 1$$

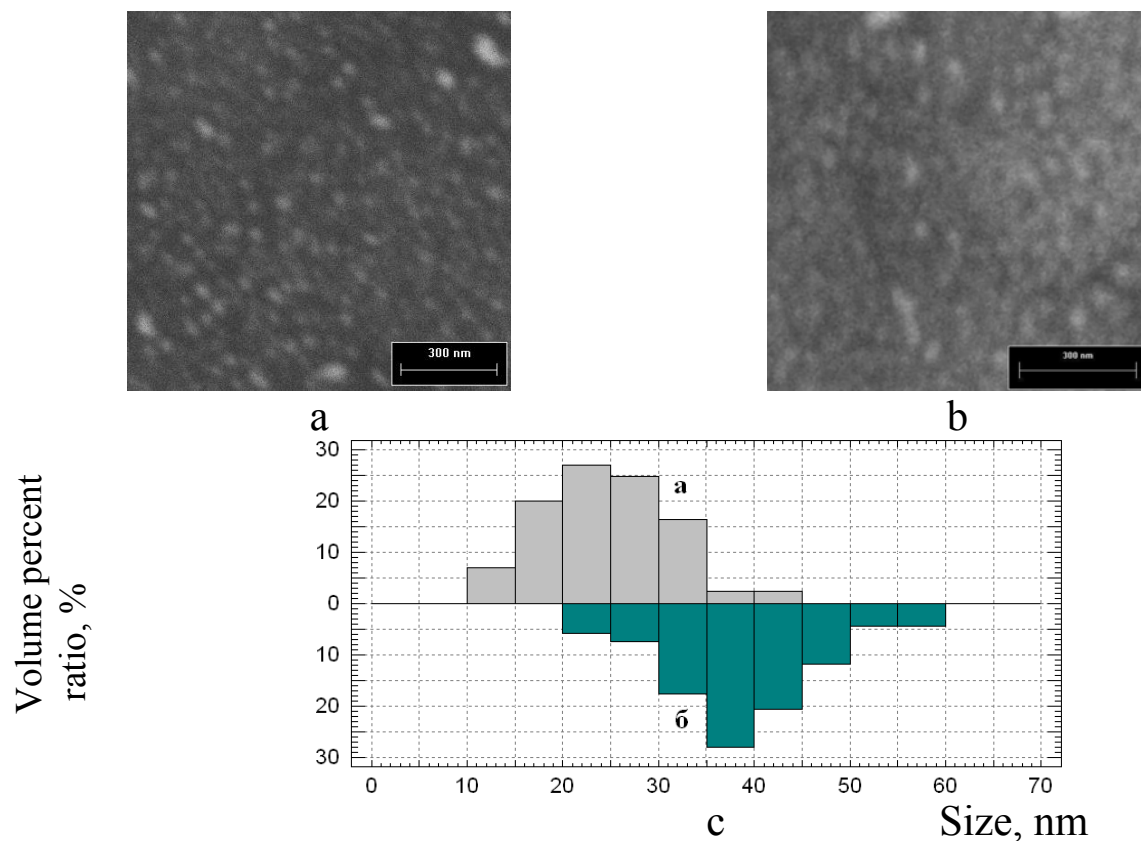
For discrete cubic particles of size  $d$  expressions (2) should be rewritten as

$$d = \frac{P_1 \cdot D}{6 \cdot f \cdot \rho \cdot n} \quad \text{eq 4}$$

#### 4. Discrete metal coatings on inorganic material powders

Many inorganic materials and coated products from combinations of chemical elements and their compounds are consolidated from initial powdered initial components (substances).

At present composite powders consisting of dissimilar weakly interacting nanosized structural components, have become important for product improvement. Discrete nanosized metal coatings on inorganic powders are characteristic examples.



*Fig. 3 Distribution of silver nanoparticles on the surface of NaCl powder:*

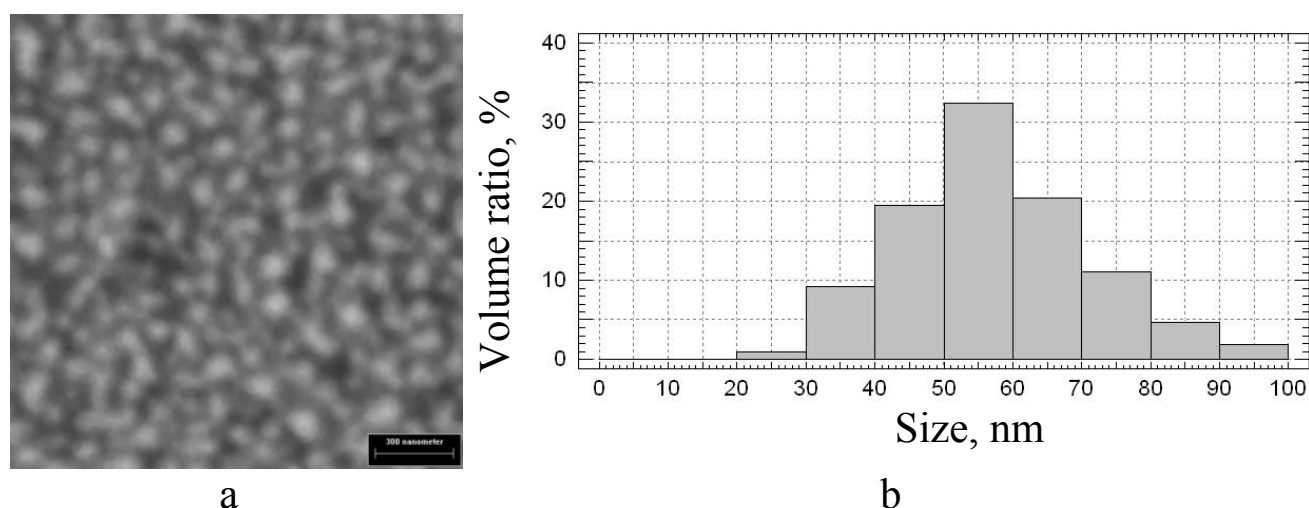
- a) discrete structure, exposure time of 3 min ( $\times 200,000$ );*
- b) discrete structure, exposure time of 10 min ( $\times 200,000$ );*
- c) histograms of size distribution of silver particles*

Fig. 3 shows discrete nanostructures of silver on NaCl powders with average size of 400  $\mu\text{m}$ . As follows from Fig. 3a, b, c average size of silver islets on powder surface depends on exposure time.

At exposure time of 3 minutes, average islet size is 25 nm (Fig. 3a). After increase of exposure to 10 minutes, islet growth up to 50 – 60 nm is observed (Fig. 3b).

Statistical histograms of size distribution of silver particles after exposure are presented in Fig. 3c. Longer exposure results in peak shifting towards greater particle size, however the general pattern of their distribution does not change, which is indicative of uniform growth of islets.

Fig. 4 shows such discrete copper coatings on NaCl powder. As



*Fig. 4 Distribution of copper nanoparticles on the surface of NaCl powder: a) discrete structure, exposure time of 10 min. ( $\times 150,000$ ); b) histogram of size distribution of particles.*

follows from Fig. 4b, average size of copper particles on powder surface is equal to 55 nm.

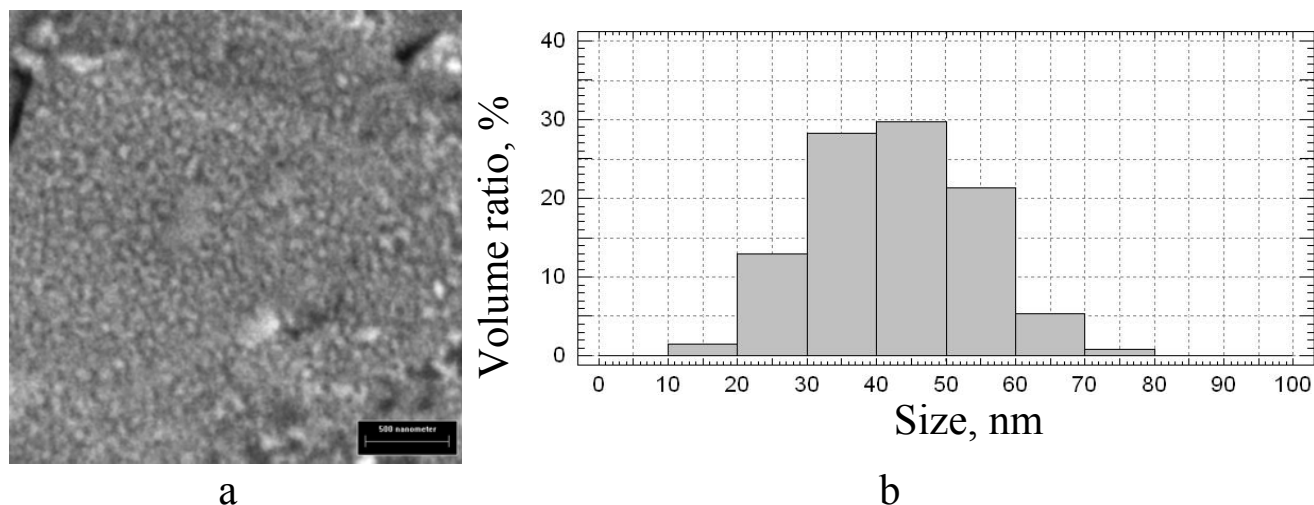
Discrete nanostructures of silver were also produced on  $\text{Al}_2\text{O}_3$  powders. Fig. 5 shows discrete nanostructures of silver. The mean size of silver nanoparticles on  $\text{Al}_2\text{O}_3$  powder surfaces was  $\sim 45\text{nm}$ .

## 5. Discrete coatings on organic material powders

### 5.1. Composite powders for colloidal systems

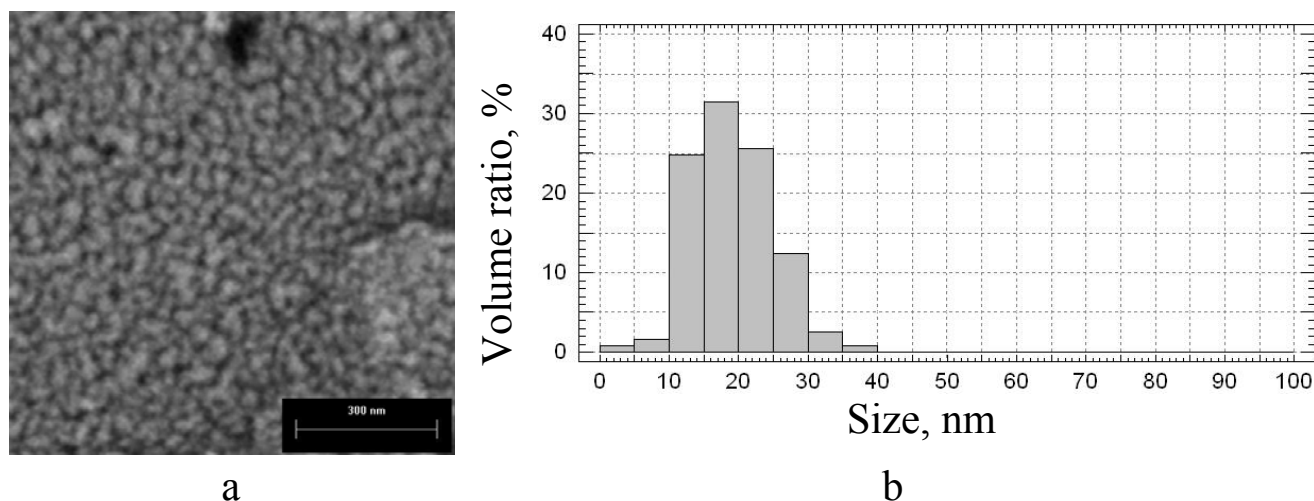
Among the colloids the most widely applied in practice are hydrosols – two-phase heterogeneous highly dispersed systems, in which water is the dispersion medium. Organosols, in which the dispersion medium is organic solvents, are also employed.

For experiments we selected the synthetic hydrophilic surface active polymer, polyvinylpyrrolidone (PVP), with molecular weight of  $\sim 30.000$ ,



*Fig. 5 Distribution of silver nanoparticles on the surface of  $Al_2O_3$  powder: a) discrete structure, exposure time of 3 min ( $\times 100,000$ ); b) histogram of size distribution of particles.*

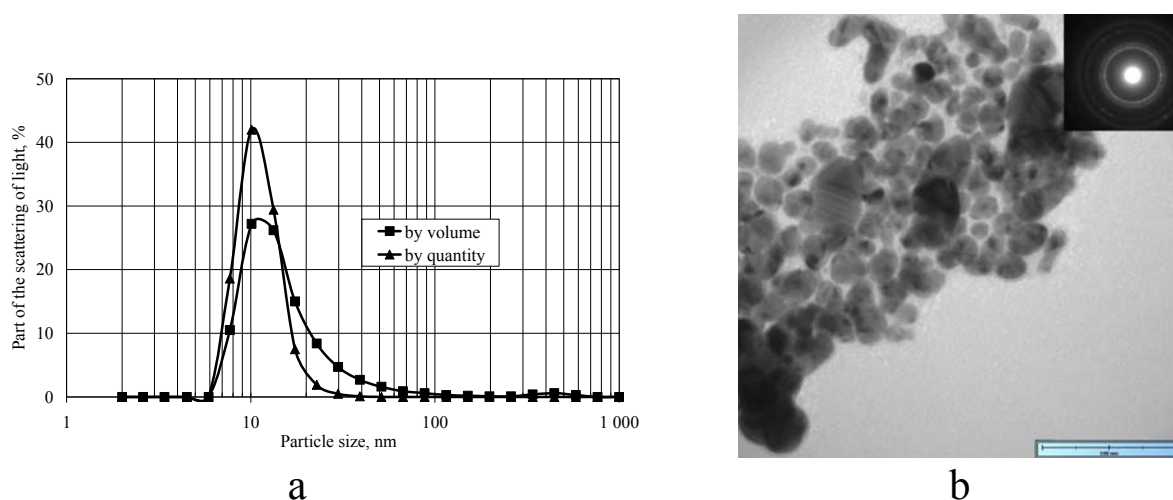
which is applied in capping pharmaceutical products as an adjuvant and active ingredient. It readily dissolves in water, as well as methanol, ethanol, glycerin, ethylene-glycol and other organic solvents. Therefore, PVP powder with metal nanoparticles is a promising composite for their



*Fig. 6 Distribution of silver nanoparticles on powder surface (PVP): a) discrete structure, exposure time of 3 min. ( $\times 150,000$ ); b) histogram of particle size distribution.*

subsequent transport into a liquid colloidal system. The structure of coating produced on PVP surface is shown in Fig. 6a, with histogram of particle distribution in Fig. 6b.

Further investigation after dissolution of powder with Ag nano particles in water, and determination of particle size using LCS and TEM is presented in Fig. 7.



*Fig. 7 Distribution of silver nanoparticles in the volume of 3% PVP-water solution:*

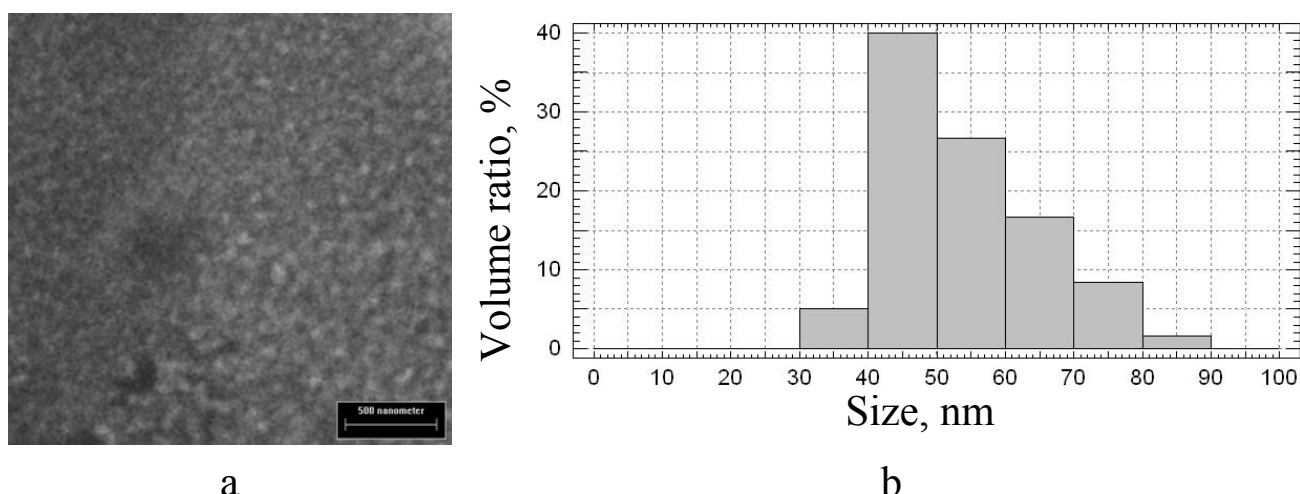
- a) curve of particle size distribution obtained with LCS;*
- b) silver particles, image produced with TEM*

Particle distribution after dissolution of powders of Dexstran-40-silver composite in water was also examined. These results demonstrate the ability to produce colloidal systems applying a simple technological cycle: EB-PVD deposition of metal nanoparticles on surfactant powders and their subsequent dissolution in the respective dispersion medium.

## **5.2. Discrete coating on drug powders**

Modification of the powder surface structure of medicinal substances and drugs by deposition of metal nanoparticles promises an improvement pathway widening of the spectrum and increasing of the level of their functional bioactivity. This is true, first of all, for isolated silver nanoparticles, the properties of which and mechanism of their positive action continue to be the focus of extensive research in many countries<sup>8-10</sup>.

Ag nanostructure coatings were deposited on existing drug surfaces by the technological procedure shown in Fig. 1d. During the entire experiment the drug powder was contained within a copper water-cooled bowl with provision for continuous stirring. The powder temperature was in the range of 30 – 50 C. Fig. 8 shows a discrete structure of silver nanoparticles on the surface of metronidazole powder.



*Fig. 8. Distribution of silver nanoparticles on the surface of metronidazole powder:*

*a) discrete structure, exposure time of 3 min. ( $\times 100.000$ );*

*b) histogram of particle distribution by size.*

Changing exposure time allows control of the islet dimensions and degree of surface filling. The average size of islets at the start of condensation was recorded by SEM, equaled 20 – 30 nm. Similar structures were also obtained on other drugs (Ceftriaxone, Streptomycin, Methyluracil).

A distinctive feature of discrete silver nanostructures on drug powders compared to inorganic powders consists in the diversity of discrete formations on powder surfaces, including acicular (thiotriazole) elements. Initial microbiological studies of drugs with modified surface confirm the enhancement of their functional bioactivity.

## **6. Directions of further research and development**

The results of technological variants of EB-PVD produced nanostructured Ag and Cu coatings on granules and powders of inorganic and organic materials, in our opinion, demonstrate confirmation of the rationality of further research and development of such coatings from additional materials evaporated by the electron beam in vacuum. For instance noble metals, Fe, Ni, Cr, Si, Ti, Ce, Zr metals, their oxides and thermally stable polymers are candidates for future studies.

Two main directions of research and development can be outlined.

1. Inorganic and organic granules and powders with coatings represent semi-finished products (substances). In order to manufacture a final product, various subsequent treatments, including consolidation with other substances or dissolution, i.e. “releasing” nanoparticles at production of colloidal systems require development.

2. Inorganic and organic granules and powders with coatings, which represent finished products; for example: catalysts, sorbents, drugs with enhanced functional bioactivity and nanovectors (particles) for targeted delivery, food additives, etc.

Currently available electron beam equipment for EB-PVD is capable of meeting these processing challenges. Fig. 9 shows the range of



*Fig. 9 Laboratory (a) and production (b) units for material evaporation and condensation in vacuum*

laboratory and production units for evaporation and condensation of materials in vacuum, which have developed and are manufactured by the International Center for Electron Beam Technologies of the E.O.Paton Electric Welding Institute of the NAS of Ukraine.

### **Instrument citation:**

Laser correlation spectrometer “Zeta Sizer-3” with multi computing correlator type 7032 ce, Malvern Instruments Ltd, United Kindom.

Scanning electron microscopes (SEM) Vega3, Tescan, USA.

Scanning electron microscopes (SEM) CamScan 4D with energy dispersive microanalysis (EDA) INCA-200 Energy, England.

Transmission electron microscopes (TEM) H-800, Hitachi, Japan.

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## **ABSTRACT**

Technological variants of electron beam vapor deposition (EBPVD) of metal coatings with nanosized structure on the surface of powders of inorganic and organic materials are examined. One EBPVD variant allows the formation of an atomic-molecular vapor flow which permits deposition on surfaces of various configurations. Nanostructure Ag and Cu coatings were used as examples to demonstrate the possibility of producing metal coatings on powders and granules. Specific attention was directed to discrete islet structures in coatings with adjustable size of islets within 5-60 nm.

Structures of coatings of medicinal preparations such a metronidazole and thiotriazoline on organic material powders:  $\text{Al}_2\text{O}_3$ , NaCl and organic substances: polyethylene, polyvinylpyrrolidone was characterized. The ability to produce colloidal systems by a simple technological procedure, namely: deposition of metal nanoparticles on surfactant powders and subsequent dissolution of the composite in water or other solvents was demonstrated.