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DETERMINATION OF THE EFFICIENCY OF PRODUCING METAL NANOPARTICLES BY EB PVD TECHNOLOGY

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ABSTRACT

Approaches to synthesis of Ag, Cu nanoparticles in liquid matrices and on the surface of both organic and inorganic powders and granules of different dispersity for biomedical purposes were analyzed. The advantages of nanoparticle synthesis by the methods of physical deposition in vacuum over the methods of chemical and hybrid synthesis are given. The high effectiveness and advantage of deposition from the evaporator with a directed vapour flow in vacuum are shown, compared to the classical crucible evaporation scheme. Optimal technological modes of deposition from the evaporator were established for achieving uniformity of the directed vapour flow. The dependence between the target temperature, efficiency of the evaporation scheme and evaporator to target distance was experimentally determined.

KEYWORDS: nanoparticles, electron beam evaporation and deposition, composites, dispersed systems, silver, copper, directed vapour flow, vacuum

INTRODUCTION

Due to the size effect, nanoparticles (NP) have unique properties, which allows them to be used as components of modern materials for a wide range of applications, such as optics, catalysis and biomedicine. Research works are carried out in the areas of diagnostic, therapeutic and prophylactic applications of Au, TiO, Ag, Cu, Zn, Si, CeO and Pt nanoparticles [1, 2].

ANALYSIS OF LITERATURE DATA AND PROBLEM STATEMENT

Today, there are thousands of different NP synthesis methods that allow obtaining stable colloidal solutions of single-dispersed NP and discrete coatings with NP on powders and granules. However, not all presented synthesis methods are suitable for expanded production because of a low efficiency, poor reproducibility or complex purification processes [3–5]. The available technological variants of obtaining such systems with a certain degree of conditions can be divided into three main groups: chemical, physical, hybrid (bio-assisted methods, green synthesis) [6]. Typically, chemical methods are low-cost and allow obtaining a large amount of NP. However, several disadvantages can be distinguished, among which contamination by precursor chemicals, use of solvents and formation of dangerous by-products. The so-called bio-assisted methods, biosynthesis or green synthesis also attract the attention of many researchers due to the ecological nature of these processes, which contribute to the involvement of biological systems or because they are directly related to biological systems [6–8]. These methods use, among other things, bacteria, fungi, viruses, yeast and plant extracts for NP synthesis. Although biological procedures are very promising, the main problem is the reproducibility of processes. In addition, the exact mechanisms, which are the basis of NP formation with the help of green plant extracts, are still not clarified. Physical methods are valuable because they are free from contamination with solvents, reducing agents and other reaction products [9]. However, the rate of production is relatively low, and the cost of production is very high, mainly due to the power consumption to maintain the necessary pressure and temperature conditions used in the process of synthesis. The methods of chemical synthesis and mechanical grinding do not fully meet the requirements to obtaining chemically pure NP metals. The most promising among the physical methods used for NP synthesis are methods based on the vapour phase condensation (VPC), which can be classified taking the power source as the basis. They include methods of magnetron, electrical discharge, pulsed-arc, ion-plasma synthesis, etc., among which electron beam exceeds all the mentioned sources by the specific power capacity, ease of control, efficiency and locality of heating. It should also be noted that despite the relative chemical purity of obtained nanoparticles, VPC methods have a low efficiency inherent in most physical methods. Since the formed vapour flow is distributed according to the law (cos φ) throughout the whole volume of the working chamber, it leads to undesirable consumption of condensing material, especially during the synthesis of nanoparticles from expensive metals (Cu, Ag, Au, Pt), and also to some extent limits the list of materials, that can be used as a target (liquids, powders) [10]. In [10, 11] it was demonstrated that it is possible to use electron beam evaporation with the subsequent deposition in vacuum (EB-PVD) by means of an evaporator and a steam line, which allows directing the vapour flow directly to the target at an angle of 45°. The use of an evaporator with a vapour flow direction at an angle of 90° can increase the evaporation efficiency and increase the reproducibility of the NP synthesis process. In [12, 13], the possibility of using the EB-PVD method with a directed vapour flow for the synthesis of Ag and Cu nanoparticles in the size range of 20–40 nm in liquid matrices based on monomers, precursors of polyurethane, fatty and synthetic oils was demonstrated. Also the possibility of producing discrete coatings from Ag and Cu nanometer size on powders and granules of different dispersion [14] and medical bandages was presented [15].

AIM OF WORK AND TASKS OF RESEARCH

is to determine the optimal parameters of the technological scheme of electron beam evaporation using an evaporator with a directed vapour flow to achieve a high efficiency and reproduction of the process of nanoparticle synthesis in the volume of liquid matrices-carriers and on the surface of powders, granules, tissues. To achieve the set aim, the following tasks were solved: to produce evaporators with the ability to direct a vapour flow at a set angle; develop a procedure and adapt electron beam equipment for determination of efficiency and distribution of vapour flow over the target surface; set the technological mode of a directed deposition of silver and copper, that will provide a high value of the efficiency and reproducibility of the NP synthesis process.

MATERIALS, EQUIPMENT AND RESEARCH METHODS

Experimental works on determination of the efficiency of the technological scheme of using evaporators with a directed vapour flow and uniformity of vapour flow distribution on the target surface was carried out in the electron beam unit UE-142. Heating of the materials and transferring them to the vapour phase was carried out by an electron gun at 20 kV accelerating voltage with $5 \cdot 10^{3}$ Pa vacuum level in the working chamber. The evaporation schemes (angular and vertical) were developed and applied with the direction of a vapour flow from the top down (Figure 1). The vapour flow was directed at a negative angle to a horizontal plane of 45 and 90°, respectively. As an evaporator material, the refractory material graphite was used. For the steam line, molybdenum was used, which has a chemical resistance at high temperatures against evaporated metals: silver and copper.

The vapour flow above the target was formed in the form of a cone. The capture of as larger volume of the formed vapour flow by the target as possible can be realized when the distance from the steam line to the target is reduced and the area (of the surface) of the target itself is increased. At the same time, the distance between the steam line and the target affects not only the efficiency, but also the heating of the target at the expense of heat transfer. The distance from the reactor steam line to the surface of the dispersed liquid was determined based on the value of efficiency, thermal effect and uniformity of the distribution of vapour flow of the metal over the target surface. The length of the steam line was chosen based on the optimal length, at which condensation of the metal from the vapour flow on the surface of the inner walls of the molybdenum tube does not occur.

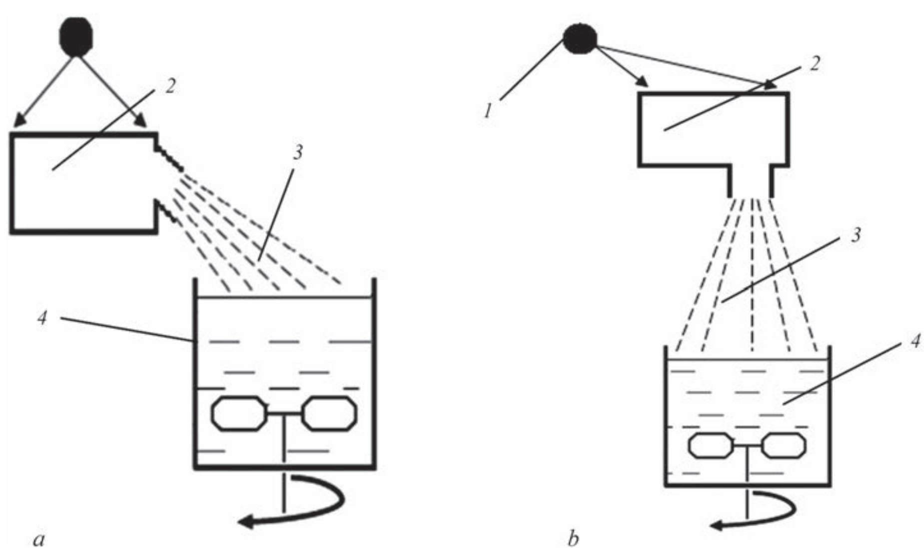

Figure 1. Technological schemes of vapour flow deposition: *a* — angular; *b* — vertical, where *1* — electron beam gun; *2* — graphite evaporator with a molybdenum steam line; *3* — directed vapour flow; *4* — liquid matrix

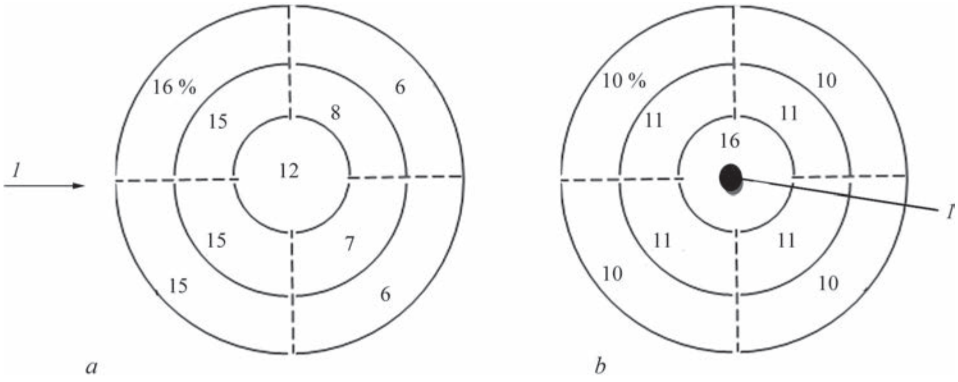

Figure 2. Uniformity of vapour flow distribution on the surface of a test copper disc, depending on the location of a graphite evaporator, %: *a* — angular scheme of vapour flow deposition; *b* — vertical one, where *1* — direction of vapour flow

The deposition was performed on the surface of a flat copper disc with a diameter of 90 mm. The size of the disc corresponded to the inner diameter of the copper water-cooling bowl, in which the target material (liquid or powder) was placed. Before deposition, the surface of the disc was cleaned and degreased with technical alcohol. The disc was arranged on the place of the bowl so that the axis of the steam line coincided with the centre of the copper disc. The distance between the evaporator and the disc corresponded to the distance between the evaporator and the surface of the liquid, powderlike target. Before placing the copper disc, it was weighed in the vacuum chamber. After conducting the experiment on the deposition of a directed vapour flow on the surface of the disc, its weight was recorded repeatedly. Similarly, before the experimental works and after, the weight of a silver weighed amount was recorded. Knowing the amount of evaporated silver and the weight gain of the copper disc, the efficiency was determined based on the proportion. Also, with the help of a chromel-alumel thermocouple, the temperature of the copper disc during the deposition process was recorded.

At the next stage of the experimental works, the process of vapour flow distribution on the target surface was determined. For this aim, witnesses were manufactured — copper flat squares of 10×10 mm. The witnesses were placed on the copper disc surface along and across the horizontal and vertical diameter of the copper disc in a 10 mm step in order to determine the vapour flow distribution over its surface. The same as for the copper disc, the weight of the witnesses was recorded before deposition and after. Having established the amount of evaporated silver, previously weighing the silver weighed amount before the experiment and after, based on the proportion, the percentage weight gain on each witness relative to the total weight gain on the witnesses was determined. On the basis of the obtained data, the diagrams of the vapour flow distribution on the target surface for both types of evaporators were constructed (Figure 2). The statistic data were processed using the computer software complex Statgraphics.

RESEARCH RESULTS AND DISCUSSION

Experimental works on the determination of vapour flow distribution over the target surface showed that the obtained results indicate a nonuniform vapour flow distribution for the angular evaporator (Figure 2, *a*). The vapour flow concentration gradient is observed along the target at an interval of 12–16 and 12–6 % for the left and right sides of the target, respectively. To the left side of the target, 67 % of the deposited material and for the right one, 33 % accounts. For a vertical evaporator (Figure 2, *b*), a gradient of the vapour flow concentration was observed from the centre to the end of the target, as was evidenced by the vapour flow distribution interval of 16–10 % for the left as well as for the right parts of the target. This indicates the relative uniformity (symmetry) of the vapour flow distribution for the left and right sides of the target and is explained by the coincidence of the steam line axis with the target centre.

The distribution of the vapour flow was determined with the help of a cover glass of the same area, the mass of which was compared before deposition and after. A series of experimental works was carried out for two types of evaporators — vertical and angular one. It was found that depending on the distance to the target, the efficiency of the evaporator with an angular orientation of the steam line ranged from 16 to 18 %, and with a vertical one was 36–40 %. Based on the fact that the efficiency of the vertical reactor is

Table 1. List of experimental data

Distance from the steam line to the copper disc surface, mm	Efficiency of evaporation scheme, %	Surface temperature of the copper disc, °C
25	61	116
45	56	72
65	40	47
85	33	41
115	22	36

2.2 times higher than the angular one, and such location provides a more uniform distribution of a vapour flow, for the further study, a scheme with a vertical arrangement was selected. The obtained experimental data of efficiency and temperature ratio of the copper disc-target depending on the distance to the target are given in Table 1.

CONCLUSIONS

1. The proposed variant of evaporators with the possibility of evaporated material (Ag, Cu) formation in a set direction of an intensive vapour flow makes it possible to reduce its consumption by 6–10 times compared to the traditional scheme.

2. It was determined that the efficiency of the evaporator with an angular steam line orientation amounts to 16–18 %, and with a vertical one it is 22–61 %. The evaporator with a vertical steam line orientation has a higher uniformity of the vapour flow distribution over the target surface compared to the angular evaporator, which provides the higher value of the reproducibility of the nanoparticles synthesis process in the volume of liquid matrices - carriers and on the surface of powders, granules and tissues. The optimum distance amounts to 70 mm, since such values do not exceed the boundary temperature and a rather high value of efficiency of the evaporation scheme.

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