Synthesis of Cu nanopowders by condensation from the gas phase

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Abstract. In order to determine the most efficient regimes of copper nanoparticles synthesis, a series of experiments were conducted by evaporation and subsequent condensation of the raw material in an argon atmosphere. During the tests it was found that an increase of evaporation rate increases significantly the average size of the synthesized particles. However, the study of the dependence of dimensional parameters of the produced clusters on the intensity of the buffer gas flow rate has encountered significant difficulties associated because the results significantly divergent from the previously conducted experiments on the synthesis of transition metal oxides. In order to solve this contradiction the computer simulation was held of copper atoms condensation from the gas phase for the three different cooling rates and for the two final temperatures $T = 373$ K and $T = 77$ K. It was found after analysis that the rate of cooling of the gas mixture and the final temperature directly influences the number and the size of particles produced. For instance, with the 10 times of cooling rate decreases the average size of the particles obtained had increased by 2.7 times at a final temperature of 77 K and by 3.1 times at $T_f = 373$ K.

1. Introduction
Preparation of stable nanoscale copper particles having unique physical and chemical properties [1], is complicated task nowadays because the metal nanoparticles are rapidly oxidized in air or aqueous environment [2]. Currently there are many ways of nanoparticles producing of transition metals, such as mechanochemical methods, plasmachemical methods, some embodiments of a chemical, photochemical and radiation reduction, and the method of condensation from the gas phase [3]. A large volume of the nanooxides is synthesized using the method high temperature pyrolysis [4], and in much less quantity by the material’s evaporation by the laser pulses in a very short femtosecond range [5].

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However, not all of the above mentioned approaches are capable to provide the required purity of the nanomaterial. Among the variety of methods, in our opinion, the most promising method for the synthesis of fine particles, including the copper particles [6], is the method of evaporation of metals by powerful electron beam and subsequent condensation of vapor in the atmosphere of inert gas. Simple scalability to industrial volumes, any material allowed to evaporate and the high purity of the resulting product with the required technical application properties (electrical conductivity, strength, ductility) distinguishes particles synthesized by a gas phase method from the particles obtained by other methods.

The huge interest, shown by researchers to study nanoscale particles of transition metals, in particular to copper clusters, is due to the fact, that a decrease in the size of up to several tens of nanometers changes significantly the fundamental properties of the material, e.g. thermal and electrical conductivity, heat capacity and reactivity. This leads to the fact that these particles begin to be widely used as a feedstock in the production of variety of ceramic and composite compounds, superconductors, electronic components, filters, catalysts [7, 8] and nano electronic devices [9]. In particular, the nanosized copper clusters, in its electrically conductive properties can compete with silver. A huge range of applications of copper nanoparticles is available in steel production and the chemical industry [1]. However, the preparation of copper nanoparticles and other metals in fairly large quantities with the necessary properties of nanoscale clusters, depending on the application, claims very high demands to the production method.

In this paper the details are described of the copper nanoparticles synthesis through metal evaporation by the high energy electron beam in inert atmosphere to determine the most efficient modes of obtaining the material with the required size distribution at the suitable productivity of installation. The significant difficulty of the experimental study is impossibility to observe the processes of particles growth and their structuring. The materials obtained by this method are studied only after the synthesis process, without a complete understanding of the physical picture of the formation of nanoparticles. The computer simulation using a physically-based interatomic interaction potentials allows to identify the main patterns of nucleation, nanoclusters growth, consistent and zero-defect formation of coordination shells, structural isomeric transitions and morphological features of cluster surfaces. Therefore, in this paper, experimental study of copper nanoparticles condensation from the gas phase was complemented by molecular dynamics simulation of the cooling of 85000 of copper atoms system. This computer model was created in such a way to reflect maximally the processes which occur in a real experiment on the evaporation and condensation of nanoparticles.

In this paper, the condensation of copper nanoparticles was carried out on experimental-industrial facility jointly developed by the Khristianovich Institute of Theoretical and Applied Mechanics and Budker Institute of Nuclear Physics of SB RAS (Novosibirsk). The facility based on the linear electron accelerator ELV-6 with the release into the atmosphere of the focused relativistic beam with an energy of 1.4 MeV and power up to 100 kW. Such energy level allows to work at atmospheric pressure of gas flow because scattering losses in the gas are small.

On the basis of the processes occurring at the experimental-industrial installation the computer model had been built of copper nanoparticles condensation after high-temperature evaporation of raw material. A model system was a cube volume of $42600 \text{ nm}^3$ containing 85000 copper atoms uniformly distributed in space, with an initial temperature $T_i = 1000 \text{ K}$. Due to the large number of atoms in the system, it was decided to model clusters condensation not in inert gas atmosphere, but for its model, in which the gas environment consists of the virtual particles having a constant temperature and generated by Andersen thermostat [10]. This thermostat allows the cooling with a fixed speed by gradual removing of excess energy from the system. To find a solution to the equations of motion of the particles in the model block the Verlet scheme was used in its "speedy" form [11] with a constant time step ($h = 2 \text{ fs}$).
2. Results and discussion

In the present study we examined the effect of the main parameters such as the electron beam power, flow rate of the buffer gas and the temperature of coolant on the final shape and size of copper nanoparticles. To date, there are several methods for determining the size of the synthesized nanoparticles. For example, direct, but at the same time a very laborious method (even if the modern image processing software is available) is the averaging data of transmission electron microscopy (TEM). It allows also to get the estimation of the nanoparticle size distribution. However, the simpler and faster way to determine the average particle size is the specific surface measurement, which is calculated for spherical particles from the expression \( S_{\text{sp}} = \frac{6}{d \cdot \rho} \), where \( d \) - the average particle diameter, \( \rho \) - density of the particle material. The specific surface area is readily determined by nitrogen adsorption with the BET method. Then it is possible to calculate \( d \), as an integral parameter characterizing the size of the primary nanoparticles of powder and promptly judge the optimal conditions for obtaining particles with the specified parameters. For non spherical complex particle the average size can be obtained using by special approaches approximating experimental measurements [12]. So, in our research the size parameters (in particular during debug series) were investigated by measuring the specific surface of nanopowders, and the TEM was also used for mutual verification.

Table 1. The structure and the shape of Cu nanoclusters synthesized from the gas phase

| Cooling rate (U, ps\(^{-1}\)) | Temperature (T, K) | Number of clusters | Average cluster size | Structure | Form |
|-----------------------------|-------------------|-------------------|----------------------|----------|------|
|                             |                   |                   |                      | FCC (HCP), % | Ih, % | Dh, % | Amorphous, % | Worm like, % | Spherical, % |
| 0.05                        | 77                | 46                | 1847                 | 22.02     | 45.83 | 20.87 | 11.28        | 76.08        | 23.92          |
| 0.025                       | 77                | 35                | 2428                 | 22.51     | 41.93 | 30.02 | 5.54         | 74.28        | 25.72          |
| 0.005                       | 77                | 17                | 5000                 | 23.59     | 26.82 | 49.59 | 0            | 58.83        | 41.17          |
| 0.05                        | 373               | 19                | 4473                 | 22.57     | 31.38 | 46.05 | 0            | 89.47        | 10.53          |
| 0.025                       | 373               | 13                | 6538                 | 29.43     | 30.07 | 40.5  | 0            | 84.61        | 15.39          |
| 0.005                       | 373               | 6                 | 14166                | 38.33     | 26.67 | 35    | 0            | 83.34        | 16.66          |

In our experimental research the possibility had been proved of particle size distribution control by varying the electron beam power and by flow rate of the argon. With the irradiation power the value of specific surface of the nanoparticles decreases (i.e., the average size increases). This is due to the fact that in the process of particles formation the concentration of vapor significantly increases. And, the higher gas flow rate leads to faster cooling rate, that eventually leads to a decrease in their average size. The experimental results were compared with calculations. The molecular dynamics simulation of copper atoms condensation from the gas phase was made for three different velocities \( U = 0.005 \text{ ps}^{-1} \), \( U = 0.025 \text{ ps}^{-1} \) and \( U = 0.05 \text{ ps}^{-1} \) (corresponding to a cooling rate of about \( 10^5 - 10^6 \text{ K/s} \)) and two end temperature \( T = 373 \text{ K} \) and \( T = 77 \text{ K} \).

During the simulation of the atoms condensation process the temperature in the system is determined by two independent factors, such as vapor cooling rate and the thermal energy coming from atoms bonds energy. The condensation of the copper atoms in this model takes place very rapidly. In first few picoseconds of condensation the atoms combine into small cluster fragments, what leads to a significant increase of the kinetic energy in the system, which will undoubtedly entail a sharp jump in temperature. This effect is difficult to observe in the direct experimental studies, but the it makes a significant contribution to the further dynamic growth of the particles.
The cooling rate of the atomic vapor is determined by the frequency of collisions and by the difference between the atomic masses of coolant and of metal atoms. In our case, as mentioned above, as the cooling buffer gas the virtual particles generated by Andersen thermostat are used. The use of this thermostat allows very rapidly to withdraw the excess kinetic energy from the system by means of elastic collisions of virtual particles and metal atoms.

As a result of the six options of modeling of copper atoms condensation from the vapor phase (with three different values of the cooling rate and the two end temperatures), a detailed analysis of the simulated systems in the last stage of the synthesis was conducted. In particular, we studied the effect of variable parameters on the amount, structure and shape of the particles obtained (Table 1). It is clearly seen that the rate of cooling of the gas mixture directly affects the number and average size of the clusters in the system provided the same number of atoms (85000).

By reducing of the cooling rate in 10 times the average size of the particles increased in 2.7 times at a final temperature of 77 K and 3.1 times at $T_f = 373$ K. In addition, in the system cooled to liquid nitrogen temperatures, approximately two and a half times more particles are originated than in the system cooled to the boiling point of water. This dependence is quite natural, and, as previously mentioned, is associated with an excess of kinetic energy in the system using cooling water. The size of the particles in the computer experiments varied from a few to tens of nanometers, and the particles synthesized under such a condition could be formed by combining each other of more than 20 small primary clusters (Figure 1).

As a result, the process of experimental synthesis of copper particles the clusters are formed of similar chain shape, but with a much larger size. The formation of large particles in the experiment is associated with technological features of the experimental setup, in particular with the the method of collecting of the synthesized particles on the fabric filter, what leads to a significant increase in the size of the synthesized particles. As an example, Figure 2 shows the experimentally synthesized copper clusters having a pronounced worm-like shape, what is similar obtained by the simulation (Figure 1).

**Figure 1.** Examples of copper nanoclusters synthesized from the gas phase at a cooling rate $U = 0.005$ ps$^{-1}$ and a temperature $T_f = 373$ K, $N = 37140$ atom.

**Figure 2.** TEM of copper nanoparticles condensed from the gas phase.
3. Conclusions
Investigation of processes for copper nanoparticles production by the evaporation of the source material by an electron beam in an inert gas atmosphere and with following condensation was conducted to determine the best mode of synthesis of the material with the desired physical properties. During the experiment it was found that with increasing of the radiation intensity the average size of the synthesized particles is significantly increased. However, due to significant difficulties in interpreting the results of studies of the effect of the buffer gas flow rate on the distribution of the nanoparticles size distribution, the molecular dynamics simulation was carried out of condensation of copper nanoparticles for the different cooling rates and final temperatures.

As a result of computer simulation it was discovered that the cooling rate of the gas mixture and the final temperature directly affects the number and size of the particles of the system, provided the same number of atoms. Since the cooling rate decreases 10 times the average size of the obtained particles increased 2.7 times at a final temperature of 77 K and 3.1 times at $T_f = 373 \, \text{C}$. The experimental investigation results show the increase in the average size of the copper particles with increase of the cooling rate system may be connected with the eddy currents under the sublimator cover causing coalescence of small droplets before leaving the crucible by prolonged residence time therein. In general, this problem can be overcome through structural improvements of sublimator.

Under the computer experiment the influence of different final temperatures on the shape of the resultant particles was investigated. As a result of the conditions identified of the predominant formation of the clusters with wormlike and spherical shapes. The production of the spherical clusters can be performed most efficiently in a system with the coolant temperature of the order of 77 K, and a vermicular clusters form at the higher cooling temperature ($T = 373 \, \text{K}$).

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