Development of plasma reactor design for synthesis of copper nanoparticles using multi-scale simulation

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Abstract. On the basis of the hybrid hydrodynamic model for the gas discharge, numerical experiments were performed. The main parameters of the electric discharge of a direct current with copper cathode and anode were obtained. The obtained data were used as the main conditions for molecular-dynamics simulations of the copper vapor nucleation process in the argon. The results of the simulation formed the basis for the development of an experimental setup for the plasma synthesis of copper nanoparticles.

1. Introduction
The search for new methods for the synthesis of metal nanoparticles is an actual problem for modern science. First of all, this is due to the widespread use of them in various fields of human activity. Particular important is copper nanoparticles biomedical applications [1].

This work is devoted to the simulation of the processes leading to the formation of copper nanoparticles in an electric DC microdischarges and developing particle synthesis reactor designs. The possibility of the formation of conditions for the formation of metal nanoclusters in the gas discharge is due to the bombardment by high-energy ions of the electrode surface and the release of individual atoms of copper in the interelectrode space [2, 3]. Two main stages of simulation with different spatial and temporal scales were implemented. The simulation data allowed us to identify the optimal parameters for the design of the main parts of the experimental setup for the synthesis of copper nanoparticles.

2. First simulation stage
The first stage is based on the extended hydrodynamic model [4], which describes a gas discharge of direct current in a wide range of currents. It includes the continuity equations for the concentrations of charged (electrons, ions) and excited particles, the continuity equation for the electron energy density, the heat equation for determining the temperature of heavy plasma particles (ions and neutrals). The self-consistent electric field is determined from the Poisson equation for the potential. At the cathode, both secondary electron emission of electrons and thermal emission from its surface were taken into account according to the Richardson-Dashman formula [5, 6]. Numerical simulations were performed for a current range from 10 mA to 10A. As the material for electrodes copper was used. For the heat
balance equations for the electrodes on the axis of symmetry of the cathode was put condition of zero heat flow, and on the outer walls of the cathode ($z = c$ and $r = R$) the following conditions are considered. The outer (opposite to the discharge volume) of electrode wall, maintained at a constant temperature, and electrodes sidewalls cooled by heat exchange with the ambient.

As an example, fig. 1 shows the parameters of the discharge, in case of reaching the melting point of the cathode surface, which was performed at a current of 470 mA. In this case, the discharge burns in the abnormal glow mode, the main mechanism for maintaining the discharge is the secondary electron emission. The current of thermoemission is less than the current of secondary emission of electrons by more than two orders of magnitude. From fig. 1a, it is seen that conditions are realized at the cathode under which a mixture of argon gas and copper vapor heated to a high temperature can form. Moreover, if this mixture is removed from this hot zone to the cold region, for example, by organizing a supersonic cross flow of cold argon [7], then conditions arise for the intense condensation of copper vapor and the formation of nanoparticles. Thus, a temperature value of 10,000 K and a pressure of 150 Torr can be used as input for MD simulation of the processes of nucleation and growth of copper nanoparticles.

![Image](image1.png)

**a)** Gas temperature distribution, the temperature of the cathode and anode in the discharge at a pressure of 150 Torr and a current of 470 mA.

**b)** The distribution of the sum of all types of ions $\text{Ar}^+$, $\text{Ar}_2^+$, $\text{Ar}_3^+$ in the discharge at a pressure of 150 Torr and a current of 470 mA.

Fig. 1.
3. Second simulation stage
At the second stage, using the freely distributed software package LAMMPS \cite{8}, MD simulation of the formation of copper nanoparticles under discharge conditions was carried out. The simulation was carried out with 2000 particles (atoms) of argon and copper in a 1:1 ratio. At the initial moment, the atoms were located in the computational domain in a random order. The particle concentration was chosen on the basis that at a temperature of 1000 K the pressure in the system will be about 150 Torr. The initial temperature of the system was 10,000 K, then the temperature decreased and was maintained at 1000 K for 1.2 μs, which corresponded to $6 \times 10^8$ time steps of 2 fs. The time step was chosen so that temperature fluctuations during the calculation time did not exceed 5%. The interparticle interaction of argon-argon and argon-copper was set by Lennard-Jones potential with parameters for argon \cite{9}, the interaction of copper-copper was set by the EAM-potential \cite{10}. In fig. 1 a-e shows the computational domain at time 0; 0.3; 0.6; 0.9 and 1.2 μs, respectively. It can be seen that the main stage of the formation of stable clusters occurs in the first 300 ns. In fig. 1 f it is possible to see the models of clusters formed by the moment of time 1.2 μs. The diameter of the largest cluster of 500 atoms was about 5 nm.
4. Description of experimental installation

The components shown in fig. 3, of the installation are placed in a vacuum chamber and air was pumped out, after that, the chamber was filled with an inert gas – argon to required pressure. The electrodes were connected to a power source. To initiate the discharge, it is necessary to short-term contact of the electrodes and their subsequent rupture. After the discharge is initiated, the atomized electrode material is carried away by a transverse flow of inert gas, which is fed through the nozzle. The electrode material, leaving the discharge area, is cooled, collected in the form of nanoparticles and enters the catcher. The nozzle is necessary for the formation and direction of the inert gas flow directly into the discharge area. For the experiment, copper rods with a diameter of 4 mm were used as electrodes. The system for setting the parameters of the installation in a wide range is provided for the purpose of implementing physical conditions obtained from the simulation data in the interelectrode space.
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References
[1] Imran M and Rehan R 2017 Synthesis, Characterization, and Applications of Copper Nanoparticles *Analytical Letters* **50** pp 50-62
[2] Nie M, Sun K and Desheng Meng D 2009 Formation of metal nanoparticles by short-distance sputter deposition in a reactive ion etching chamber *Journal of applied physics* **106** 054314
[3] Sadikov K G, Sofronitskiy A O and Larionov V M 2017 The effect of electrically conductive additives on the plasma pyrolysis of heavy hydrocarbons *Journal of Physics: Conference Series* **927** 012046
[4] Saifutdinov A I, Fairushin I I and Kashapov N F 2016 Analysis of various scenarios of the behavior of voltage–current characteristics of direct-current microdischarges at atmospheric pressure *JETP Letters* **104** pp 180–185
[5] Raizer Yu P 1991 *Gas Discharge Physics* (Berlin: Springer)
[6] Benilov M S 2008 Understanding and modelling plasma-electrode interaction in high-pressure arc discharges: a review *J. Phys. D: Appl. Phys.* **41** 144001
[7] Saifutdinov A I, Timerkaev B A and Zalyaliev B R 2016 Control of the glow discharge parameters at low pressures by means of a transverse supersonic gas flow *High Temperature* **54**(5) pp 632–638
[8] Plimpton S 1995 Fast Parallel Algorithms for Short-Range Molecular Dynamics *J. Comput. Phys.* **117** pp 1-19
[9] Rahman A 1964 Correlations in the Motion of Atoms in Liquid Argon *Phys. Rev.* **136** pp 405-411
[10] Foiles S M, Baskes M I and Daw M S 1986 Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys *Phys. Rev. B* **33** pp 7983-7991