The investigation of the influence of oxygen concentration in the gas mixture on nanodispersed oxides synthesis

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Annotation. Thermal effects in cathode space of low-pressure arc discharge, which contribute to the synthesis of nanopowders with an average particle size of less than 10 nm, are considered. One of the most important parameters, characterizing the cathode processes of vacuum arc, is a voltage drop across the discharge gap. All the gases demonstrate a decrease of a voltage drop across the discharge gap under the condition of increasing the gas pressure in the range of $p = 10^{-3} – 1$ Pa. Dissipation of energy of ions and electrons on gas molecules leads to rapidly heating the gas. Heat, coming from gas plasma, has a significant impact on evaporating material of a cathode. It can be assumed that a microdrop fraction, formed as a result of a cathode spraying in a liquid phase, will further evaporate in a superheated gas.

In the papers [1, 2] a method for production of nanopowders (NP) of metals and their compounds with non-metals in the plasma of a pulsed arc discharge of low pressure is proposed. Disperse powder composition is formed by means of two processes: dispersion - cooling of liquid metal and evaporation - condensation of steam phase. The studies [3-23] have shown that the obtained powder particles represent single crystals with a spherical shape. The average particle size was 10 nm.

The results clearly indicate a qualitative difference of powders, produced at different pressures of the gas mixture. The empirical formula are proposed for the dependence of a number-average diameter of the particle d_{cp} on a pressure p:

$d_{cp} = 0.3\ 10^{-6} p^{-3}$, m, at $p < 10$ Pa; $d_{cp} = 0.5\ 10^{-6} p^{-0,5}$, m, at $p > 10$ Pa

While changing the pressure in the plasma-chemical reactor, the distribution function does not change, indicating that the nature of the synthesis of electric arc powders is predominantly thermal, and particles form by condensation from vapor phase.

One of the main factors, determining the conditions of the chemical reaction, is proportion of plasma-generating and reactive gases in the plasma-chemical rector. At constant values of the parameters of electrical vacuum arc (EVA) and the pressure of the gaseous medium, the amount of the formed oxide is determined by the oxygen content in the gas.

Let’s consider the influence of this factor on the synthesis of copper oxide, taking into account the voltage drop across the discharge gap. Among the oxygen-contained components the most appropriate are air and oxygen of technical purity. The studies were carried out using the device described in [3] at a discharge current of 300 A, an intensity of the longitudinal magnetic field excited by the focusing coil on the surface of the cathode, of 80 Oe. Copper of electrolytic refining M0 was used as a cathode for spraying. The chamber was preliminary

evacuated to a pressure of 1 mPa and then it was filled by gas mixtures based on argon, oxygen and air.

The dependence of the voltage drop U on the gas pressure for the copper cathode is shown in Fig. 1 and Fig. 2. It is evident that for gas mixtures of argon-oxygen and argon-air, under the increasing pressure in the range of p = 1–10 Pa, a decrease of the voltage drop across the discharge gap occurs. Within increasing pressure of gas mixture higher than 10 Pa, a slight increasing U value is observed, which stabilizes at p = 15 Pa. Presence of oxygen and air in the system more than 5%, at p > 15 Pa, causes a sharp, almost abrupt increasing U value. While further increase of pressure above 60–70 Pa the system demonstrates instabilities and frequent interruptions of the arc discharge. For gas mixtures based on oxygen the optimal gas mixture consists of 10% O_2 + 90% Ar, the limit pressure of stable arc discharge is 60 Pa. For gas mixtures based on air the optimal gas mixture consists of 20% air + 80% Ar, the limit pressure of stable arc discharge is 70 Pa.

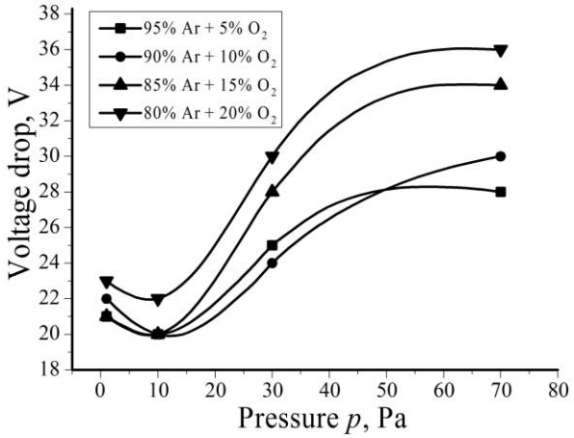

FIG. 1. The dependence of the voltage drop across the discharge gap on the pressure of the gas mixture of argon and oxygen for copper cathode

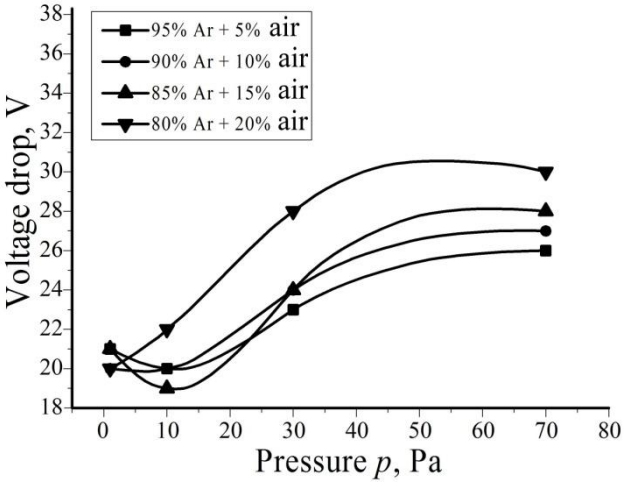

FIG. 2. The dependence of the voltage drop across the discharge gap on the pressure of the gas mixture of argon and air for copper cathode

The voltage drop across the discharge gap consists of the cathode drop and the voltage drop on the positive pole of the arc. The change of each component with the increase of p

value may have a different character and, therefore, different impact on the curves which image U values. Increase of U value under the pressure of the gas mixture $p > 10^{-1}$ Pa is caused by the processes in the arc column, which result in a decrease of conductivity of the plasma [24]: $\sigma = \frac{e^2 \cdot n_e}{m \cdot v_{eff}}$, where n_e, m – concentration and mass of the electron respectively; ν_{eff} – effective frequency of collisions between electrons and atoms.

Wherein, decrease of U value is mainly related with an increase of frequency of electron collisions with neutrals under the increase of gas pressure in the volume. In the system copper-oxygen and copper- air a sharp decrease in U value can also be associated with increase of average frequency of ion charge. These ions are generated during the formation of chemical compounds on the surface of the cathode by cathode spot of the arc. Dissipation of energy of ions and electrons on the gas molecules leads to the rapidly heating up the gas. Moreover, the increased gas concentration let to assume a significant energy content of gas in the cathode space. The heat, coming from the gas plasma, significantly influences the evaporated cathode material. It can be assumed, that the microdrop fraction, formed as a result of cathode spraying in the liquid phase, will further evaporate in the superheated gas. As known for low-temperature plasma of atmospheric pressure, the nature and intensity of the heat and mass transfer between the particles of the dispersed phase and the plasma flow will be determined by energy content of the plasma flow, the physicochemical properties of the fine phase particles, type of plasma-forming gas and, finally, a character of interaction between the plasma flow and the fine-dispersed phase, which mostly depends on the Knudsen criterion (Kn).

Heat and mass transfer in the case of Kn < 0.1 (high-pressure plasma) is most fully studied in the literature [25]. Wherein heat exchange is caused mainly by thermal conductivity and convection, and it can be described by the criterion equations, using the criteria of Nusselt, Reynolds, Prandtl, Lewis, etc. At the same time, when the character of plasma flow becomes molecular (Kn > 1), the convection processes are insignificant. Under these conditions, heat and mass transfer processes are most reasonable viewed from the standpoint of the kinetic theory. In this regard, to estimate the possibility of evaporation of microdrop fraction particles in the cathode plasma, a model based on the kinetic approach was developed. This model takes into account the fact that there is a flow of fast electrons in the cathode plasma, which are accelerated in the double electrostatic layer arising from cathode narrowing side in a compressing magnetic field. The developed mathematical model includes the equations of power balance of energy flow, which act to a body of small size, placed into the plasma of low or medium pressure, and the equations describing non-stationary heat and mass transfer in a spherical body of small size, assuming the absence of temperature gradients within the body (body was considered as isothermal). The plasma parameters in the arc evaporator, necessary for simulation, were obtained experimentally [6]. Thus, it was found that under the argon pressure in the evaporator equal to ~ 34 Pa and an anode current of about 500 A, an electron temperature is equal to $T_e = 10^4$ K, and a concentration of plasma is equal to 10^{21} m^{-3}.

The results show that the main flow of heat from the plasma to the particle is due to the energy brought by the ions. The part of the energy, brought by the electrons in the considered electronic temperature range, does not exceed 25%. Under the temperature of evaporation, the power from the powder particle is taken away entirely due to thermal radiation. The maximal temperature, to which a particle, introduced into the plasma, can be heated, is determined by the energy balance. In the above case, the copper particle temperature does not exceed 3000

K. Estimates of a time of complete evaporation of the copper particles $\tau_{исп}$ with a diameter of 55 μm at $T_c = 10^4$ K gave the value of 10^{-5} s, which is much less than the time of the copper particles existence near the plasma column in the arc evaporation at its rate of its transfer across the flow not exceeding 100 m/s.

Thus, the estimations show that, under the condition of the sufficient energy content of the plasma flow, the process of cathode evaporation in low pressure arc discharge consists of two stages: firstly the cathode material is sprayed in the liquid phase in the cathode spot, and then is completely evaporated in the near-electrode gas-vapor mixture. Furthermore, due to mixing of metal vapors with a flow of ionized carrier gas, vapors are overheated, thus preventing premature condensation of vapors and causing dissociation of the already formed clusters.

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