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Plasma-chemical synthesis of copper oxide nanoparticles in a low-pressure arc discharge

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ABSTRACT

The influence of a pressure of gas mixture (10 vol% O_2 + 90% N_2) on an average size of copper oxide nanoparticles, produced in the plasma of low pressure arc discharge, has been studied as a basic process variable. A correlation between the dependence of average particle size on gas mixture pressure and the dependence of discharge gap voltage on product of interelectrode distance by a gas mixture pressure, has been found. The estimation was carried out by means of X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). A mathematical model of the cathode region, which shows the applicability of the similarity theory to the low pressure arc discharge, has been represented.

1. Introduction

Copper oxide with nanosized particles and films are useful materials in a variety of applications such as photovoltaic devices [1,2], electrochromic devices [3], thin film transistors [4], and chemical sensors [5], owing to their moderate band gap, low cost production, and high optical transparency. Copper oxide nanoparticles are commonly synthesized by wet chemical processes [6–8]. However, it is not easy to ensure the homogeneity and crystallinity of the nanoparticles when fabricated through such methods. This is because wet chemical processes involve low temperatures. In contrast to wet chemical processes, thermal plasma-based ones involve the evaporation of the constituent metals at temperatures higher than 10,000 K, followed by the rapid condensation of the gas phases [9–13]. Thermal plasma-based processes have other advantages over wet chemical processes. One is that, using these processes, it is possible to prevent the end products from being contaminated by impurities; this is not the case with wet chemical processes [14,15]. So far, a number of thermal plasma based processes have been developed. Among them, the vacuum arc plasma evaporation (VAPE) method is commonly used for the deposition of thin films [16] and the fabrication of nanoparticles [17–22]. We recently reported that particle phases with different stoichiometries, including Cu2O and CuO, can be produced by varying the deposition conditions, such as oxygen partial pressure, discharge power, processing pressure, and substrate temperature [23].

According to the previous research, the properties of powders produced in the plasma arc discharge of low pressure, depend mainly on the gas mixture pressure in a plasma-chemical reactor [24]. Dispersion of produced powders depends mainly on two processes: evaporation and ionization of a liquid metal on a cathode surface, and condensation form a plasma-vapor phase. In a sufficiently high vacuum of ~10^{-1} Pa powder consists of particles of two types: spherical particles with size of 0.5–3 μm, wherein fine condensate dropped, and spherical particles with size of 0.5–10 μm, which represent agglomerates of smaller particles with size about 0.1 μm [24,25]. The percentage of nanopowders in this case is negligible. The experimental results clearly show the advantages of powders obtained at different pressures of the gas mixture. Change of the pressure in the plasma-chemical reactor does not lead to change of the particle size distribution function. This shows predominantly thermal nature of arc powders synthesis, where the particles are formed due to vapor condensation. The purpose of this work is to define the mechanism influencing the pressure of gas mixture in a plasma-chemical reactor on an average

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size and morphology of copper oxide nanoparticles, produced in plasma arc discharge of low pressure.

2. Materials and methods

The synthesis of CuO nanopowder was carried out in the plasma-chemical reactor described in Ref. [26]. The arc evaporator, used in the process, had the following characteristics: a current arc of 100 A, an intensity of the longitudinal magnetic field excited by the focusing coil on the surface of the cathode, of 80 A/m, a distance between the cathode and the anode of $d = 50$ mm. A rod, made from copper (99.99%) with a diameter of 80 mm and a length of 100 mm, was used as a cathode. It was placed on a water cooled copper current lead. In order to begin plasma chemical reactions, the gas of the chamber was preliminary pumped out to a pressure of $p = 1$ mPa and then the chamber was filled by gas mixture containing 10 vol% O_2 of the amount of supplied plasma-generating gas N_2. In order to study the pressure influence, nanoparticles were synthesized at basic pressures of 10, 50, 80, 140 and 200 Pa. Gas control was carried out continuously by means of a gas flow regulator and a vacuum manometer. Oxygen was supplied to the reactor in order to form a uniform layer around the plasma torch. The reaction products were collected during 10 min on a hemispherical collector made of water-cooled stainless steel, placed at a distance of 0.12 m from the cathode.

Morphological composition of the samples has been studied by transmission electron microscope JEOL JEM-2100. The analysis of dispersion distribution was performed by the method described in Ref. [27]. The study of the phase composition of the samples has been carried out using X-ray diffractometer Advance D8 in CuKα monochromatic radiation. Scanning was performed at room temperature in the range of angles at 20–120 deg with 2θ step of 0.06 deg. The microstructural characteristics and the elementary cell parameters have been determined using X-ray full-profile analysis by the Rietveld method.

3. Results and discussion

Fig. 1 shows the high-resolution transmission electron microscopy images, the diagram of particle distribution and the size distribution function of the copper oxide nanoparticles produced under the pressure of the gas mixture (10 vol% O_2 + 90% N_2) of 80 Pa.

It is easy to conclude from the above results, that the produced powder represents strongly agglomerated particles of spherical shape. The particle size ranges from 5 to 20 nm. The combination of normal and lognormal size distribution are characterized for these particles. This suggests two competing mechanisms of particle condensation from steam-plasma phase: cluster condensation and steam condensation. The mixed distribution function represents the sum of functions of lognormal and normal distribution with adjustable parameters. It can be seen from the figure above, that this function describes the particle size distribution much better. The average particle size was 9.4 nm, the mean mass particle size was 10.2 nm and the standard deviation was 1.18.

Nanopowders are characterized by high surface energy, which is balanced out by a significant aggregation of powders, which causes a significant decrease in the specific surface. It is well known [27] that particle size distribution function directly corresponds to the process of nanoparticles formation. The size distribution function can differ for various methods of nanopowders production significantly. There are two main mechanisms for nanoparticles formation: diffusive and coagulative.

While the nanoparticle chemical processes always accompany corresponding synthesis in plasmachemical reactor, the size distribution function of nanoparticles becomes more complicated because of the products of these reactions. The morphology of the particles also becomes more complicated and particles of different chemical composition are formed. Besides, reciprocal diffusion of nanoparticles in the condensed phase takes place. Under sufficiently high temperature, multiple processes can occur simultaneously, forming the strong coupling between nanoparticles. The experimental data are described by a normal distribution while prevailing the layered growth of nanoparticles due to the adsorption of atoms and diffusion processes during the atomic mass transfer at the interface [28].

Fig. 2 shows the X-ray diffraction patterns of nanoparticles synthesized at the pressures of gas mixture of (10 vol% O_2 + 90% N_2) for 2θ values in the range from 25 to 65 deg.

The diffraction patterns of nanoparticles clearly show reflexes (JCPDS data, No. 05-0667), corresponding to cuprite structure of Cu_2O, space group Pn3m. Other crystalline structures have not been found.

Fig. 3 shows the results of X-ray studies using PowderCell 2.4 software. The dependence of the average size of coherent scattering areas on the pressure of the various gas mixtures is shown.

The dependence of the average size of coherent scattering region (CSR) on gas mixture pressure is shown below. The influence of the pressure on the average size of powders was studied over a wider range of values, but this image shows only the most representative results. For example, under the pressure of the gas mixture of 1 Pa or less, the produced powders are widely ranged in size from 50 nm to 10 μm. In order to produce powders under the pressures above 200 Pa, an increase in voltage is necessary to maintain stable arcing. It causes the transition of the diffuse plasma

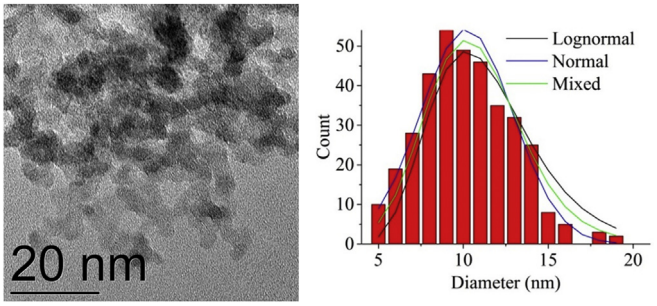

Fig. 1. TEM images, histograms and size distribution function of copper oxide nanopowders produced under the pressure of the gas mixture (10 vol% O_2 + 90% N_2) of 80 Pa.

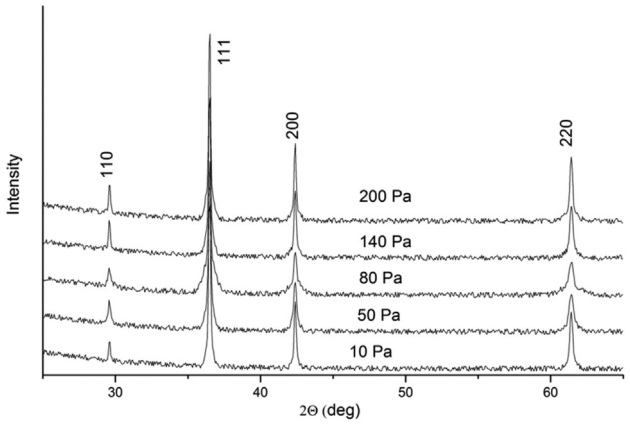

Fig. 2. The XRD patterns of copper oxide nanopowders produced at different pressures of the gas mixture (10 vol% O_2 + 90% N_2).