GASE-PHASE SYNTHESIS OF NANOMATERIALS IN CORONA DISCHARGE

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Abstract

Modified method of the gas-phase deposition of metal nanoparticles in corona discharge is studied under discharge electrode heating. The condensation of molybdenum and gold oxide nanomaterials takes place as a result of electro gas-dynamic transfer of heat electrode spraying product.

Introduction

Preparation and collection of nanoparticles is a very difficult technological process, since there is no deposition by gravity and nanoparticles are in suspension in gaseous medium. Nanoparticles are usually collected from the “cold” surface or in filters [1]. Thus, development of new methods of nanoparticles synthesis, distinguished by a high productivity, low power inputs, a single stage, easy nanoparticles methods of collection and simplicity in technological process control, is necessary.

Nowadays the methods for nanomaterials production in corona discharges of positive and negative polarities are rapidly developed. In the works [2, 3] the production of carbon nanotubes are made at the atmospheric pressure in the plasma reactor in corona discharge. Submicron gold particles, size of which is depend on the corona current, are obtained by the spraying of corona electrode material in the air [4]. The platinum particle of 10 nm deposited on SiO₂ substrate is formed by the method of electrohydrodynamic atomization in the corona discharge [5]. Corona discharge of high-temperature ionization zone and heating of the corona electrode [6–9] expands the range of produced nanomaterials and increases the process of productivity.

Experimental procedure

In this paper the synthesis of nanoparticles research in corona discharge are produced by the following scheme: 1) a required gas medium containing oxygen or chlorine is created in the discharge gap; 2) corona discharge electrode is heated by an external current source to the temperature of the evaporation of oxides or chlorides, and the evaporation temperature must be less than the melting point of discharge electrode; 3) a voltage is applied to the discharge gap, and the corona discharge is ignited; and 4) evaporating reaction products obtain similar charges, move by electric field to “a cold electrode” and deposit on it as nanoscale formations.
For synthesizing nanoscale molybdenum oxide the corona discharge is ignited in the coaxial discharge cell having a radius of outer duralumin electrode \( R = 28 \) mm, length of \( 30 \) mm, and the radius of the corona molybdenum electrode is \( 0.2 \) mm. To avoid the negative impact of the gas convective motion, resulting from the heating electrode gap on the axial symmetry, the discharge cell is oriented vertically. The corona electrode heating to \( 1500 \) °C is achieved by an extra current source.

A rise in corona current is accompanied by increase in temperature to \( 900 \) K, that in agreement with a known mechanism of corona discharge development [3]. At a higher temperature there is an active formation of molybdenum oxides, which are charged by the similar with electrode during evaporation. Oxide particles are detached from the electrode surface and moved towards the opposite electrode under electric field effect. The charge transfer within the electrode gap, along with electrons and ions of the gaseous medium, is carried out by charged particles of molybdenum oxide. Since the mobility of these particles is smaller than the mobility of electrons and ions, the decrease in the corona current is observed. Increasing a number of molybdenum oxide particles is involved in charge transfer by increasing temperature. A gradual lock of corona and a decrease in more than 3 times in the current corona discharge take place in comparison with the currents observed prior to the sublimation of molybdenum oxide particles. In cases of positive and negative polarities the corona current tends to the same value when locking. At the closing stage of the corona discharge the current transport through the discharge gap is probably mainly due to the charged particles of molybdenum.

![Fig. 1. Dependence of corona discharge current with positive (I) and negative (II) polarity on filament current (a) and temperature (b) of corona electrode under voltage of 16 kV](chart.png)
Optical microscopy of the deposited oxide (Fig. 2) shows there are “islands of aerogel-like inclusions MoO$_3$” between the dendritic formations of "whitish color". Electron microscopy (Fig. 3) allows distinguishing separate clusters of molybdenum oxide, forming an amorphous aerogel-like structure. Content of MoO$_3$ is 85 % in deposition products and for its structure amorphous structure of aerogel-like molybdenum trioxide is possible.

The corona electrode from chemically pure gold heated by an external current source up to required temperature is used to get gold nanoparticles. Chemically pure aluminum electrode is put at a distance of 4 cm away from it. For ignition of corona discharge a high voltage in the range of 0 ÷ 15 kV is applied on aluminum electrode with respect to gold. The electrode system is located in a hermetic chamber. Atmospheric air, saturated with water vapor and carbon tetrachloride, is pumped through the chamber with a fixed rate of flow. In the presence of atmospheric oxygen and water vapor near and on the surface of the electrode the filament heating over 300 $^\circ$C initiates hydrolysis reaction of carbon tetrachloride to phosgene, hydrogen chloride and chlorine:

\[
\text{CCl}_4 + \text{H}_2\text{O} \rightarrow \text{COCl}_2 + 2\text{HCl}, \text{COCl}_2 \rightarrow \text{CO} + \text{Cl}_2.
\]

Chlorine generates gold chloride on the surface of electrode:

\[
\text{Au} + \text{Cl}_2 \rightarrow \text{AuCl}_3, \text{AuCl}_3 \rightarrow \text{AuCl} + \text{Cl}_2, \text{AuCl}_3 + \text{CO} + \text{H}_2\text{O} \rightarrow \text{Au} + \text{CO}_2 + \text{HCl},
\]

that sublime and obtain charge of the same name with sign of electrode voltage. In the electric field of corona discharge the charged gold chlorides drift towards the aluminum electrode through cold outer discharge zone and on the aluminum surface reduce to metal gold:

\[
\text{Au} + \text{AuCl} + \text{AlCl}_3 + \text{Al} \rightarrow \text{Au} + \text{AlCl}_3, \text{AlCl}_3 + \text{H}_2\text{O} \rightarrow \text{AlCl}_3\cdot6\text{H}_2\text{O}.
\]

Due to local inhomogeneities of the electric field near the electrode surface and turbulent gas motion, nanoscale clusters of gold are formed on aluminum.

**Fig. 2.** Overview of deposited molybdenum oxide

**Fig. 3.** Synthesized molybdenum oxide in transmission electron microscope
In the experiments they are observed on the catalytic decomposition of hydrogen peroxide on the surface of the aluminum electrode.

**Fig. 4.** Dependence of oxygen precipitation rate on time for different experiment conditions: 1. original sample; Aluminum etched in pairs of HCl; 3. Disk under floating potential; 4. Sample treated in a positive corona; 5. Disk treated in a negative corona.

On the surface of activated alumina during activation the decomposition of peroxide on the side of aluminum chloride may occur at reaction of hydrogen peroxide decomposition. A pure aluminum is not an active catalyst for the peroxide decomposition, but its impurities contribute to the kinetics of the process. The following kinetic dependences are compared: 1) hydrogen peroxide decomposition for initial aluminum; 2) aluminum treated in the vapor of hydrochloric acid; 3) in the activation chamber without potential supply; 4) sample treated in a corona positive; and 5) the activated sample in a negative corona. As follows from the results (Fig. 4), on samples of 1–3 products of hydrogen peroxide decomposition is negligible small and their number is reduced to almost zero during the etching of more than 50 minutes. On the 3 sample, which was in the chamber during activation out of the electric field, the volume of hydrogen peroxide decomposition in comparison with the 1 and 2 samples is larger, and in comparison with the 4 and 5 activated samples is negligible. It shows the absence of catalytic affect of aluminum chloride on decomposition. Comparison of the decomposition rate of hydrogen peroxide in the samples, activated in the positive 4 and negative 5 coronas, show that the catalytic activity of the 5 sample is much higher. This behavior is explained by effective
charging of the gold chloride clusters, formed near the corona electrode in the negative corona discharge. Since there are no ionization processes in the outer zone of the positive corona discharge and the positive ions of gold chloride are unlikely to appeared, than in the positive corona the neutral gold chlorides couldn’t be transformed by electric field to the sample surface and they are carried out by gas flow from the deposition zone.

Fig. 5. The kinetic dependences of the hydrogen peroxide decomposition for samples with different time of activation.

The temperature of corona electrode and the decomposition time appreciably affect the rate of decomposition of hydrogen peroxide. Comparison of the kinetic dependences of the hydrogen peroxide decomposition in the samples obtained within different temperatures of the corona electrode shows that the maximum catalytic activity of aluminum samples is observed at the discharge electrode 300 °C. In assessing the impact of deposition time on the catalytic activity the main indicator of activity is the amount of oxygen, liberated by the decomposition of hydrogen peroxide into oxygen and water. Figure 5 shows that the activation time significantly affects the kinetic characteristics of hydrogen peroxide decomposition.

Conclusion remarks
The modified method of gas phase decomposition of gold significantly alters the physical and chemical characteristics of the aluminum surface, primarily passive to hydrogen peroxide. There is a pronounced expression of the catalytic activity of aluminum in respect of the hydrogen peroxide decomposition into oxygen and water. The conditions for maximum catalytic activity of the aluminum surface are defined. They are a corona discharge of negative polarity; filament temperature of 300 °C; surface activation time is 10 minutes.
References


