Radio Frequency Plasma Modification and Physicochemical Properties of Electrochemically Produced Co Nanoparticles

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Abstract. With the help of the TEM and XRD methods, Co sediments produced by an electrochemical method and then modified with RF discharge have been studied. Aggregates with dimensions up to 800 nm are found to be prevailing in the sediment before RF modifications, and branched chains consisting of particles 60–80 nm in size are found after modification. The main phase in the sediments is Co in the hexagonal and cubic modifications.

1. Introduction

Interest in the technology of chemical synthesis of nanoparticles is related, in particular, to attempts by reducing the size of structural elements to solve the problem of obtaining materials with a homogeneous structure and predictable properties [1]. The main factors determining the specific properties of nanoparticles in comparison with traditional materials of the same chemical composition are their size, shape, and surface condition. One of the most promising at present is an electrochemical method for producing nanoparticles of metals and metal oxides [2].

To make the special properties of nanoparticles, their surface can be modified [3], for example, by treatment in a plasma-chemical reactor by radio-frequency discharge in a gaseous environment; however, the mechanisms of such a modification have not been adequately studied [4].

In this work, we investigated the modifications in RF discharge of cobalt nanoparticles obtained by electrochemical reduction of cobalt (II) ions from electrolyte solutions on a suspended aluminum substrate [2].

2. Experimental

The experiments were conducted on samples of dispersed Al (99.0%); analytical grade CoCl₂ without further purification was used as the primary reagent. Dispersed Al was suspended in a solution of cobalt chloride (II). After the reaction, the resulting precipitate of cobalt was separated from the solution by magnetic separation, washed with doubly distilled water until neutral, then washed with ethanol and dried in a vacuum. Remains of aluminum were removed by further treatment of the precipitate with a NaOH solution (3.0 M). Part of the resulting powder material was subjected to further modification of the plasma at a pressure of the orifice gas (argon) of 26 Pa for 10 min.

The schematic of the experimental vacuum RF plant for plasma modification of nanopowders is shown in Fig. 1 [5]. The plant consists of high-frequency generator 1, chamber 2 with pumping system and vacuum diagnostics, and glass plasma reactor 3, in which the excitation of the discharge occurs.
and the plasma treatment of the material is carried out. Capacitive discharge between electrodes placed in the reactor is excited by a powerful (60 kW) generator operating at a fixed frequency of 13.56 MHz. Generators through 75Ω coaxial and 300Ω parallel lines are matched to the capacitive load of the plasma. In the absence of a match or in the formation of a standing wave in the feed line, the power developed by the generator is allocated in the feeder without being absorbed by the plasma. The chamber is evacuated by two NVR-5DM vacuum pumps and a DVN-50 rotary pump. To remove the heat load, the electrodes and vacuum chamber are water cooled.

![Experimental setup for plasma treatment of powders in RF discharge](image)

**Figure 1.** Experimental setup for plasma treatment of powders in RF discharge: (1) high-RF generator; (2) vacuum chamber; (3) reactor with material being treated; (4) electrodes; (5) compressed gas bottles; (6) capacity of steam saturation; (7) rotator with holder; (8) pumps; (9) bias voltage source; (10) adjusting valves.

Treatment of nanopowders in a capacitive RF discharge was carried out by rotating and shaking the reactor, facilitating mixing of the particles and the formation of a fluidized spatially distributed system. Entrainment of nanoparticles from the reactor through its throat is prevented by a membrane (filter), and to reduce the flow of particles toward the throat, a negative electrical potential (bias voltage) is applied to a metal mesh located next to the filter.

Reactor 3 with a loaded powder and filter set on the throat was mounted on a rotating device in chamber 2 evacuated to a pressure of 0.1—1.0 Pa, in which the orifice gas was fed through an inlet valve. After achieving a steady flow of gas and chamber pressure of 10—50 Pa, an RF discharge was excited in the plasma reactor and processing of the material was carried out.

X-ray diffraction studies of powder samples were carried out by the Debye—Scherrer method using a D8 ADVANCE (Bruker) diffractometer in monochromatized Cu Kα radiation in the scanning mode with a step of 0.02° in the range of angles 2θ = 3°—95° at the time exposure at each point of 1 s. Samples were prepared by pressing the powder in a disk cell made of quartz glass; the speed of rotation of the samples during the survey was 1 s⁻¹. The interplanar distances were calculated by the EVA program.

Identification of crystalline phases was carried out by comparison of the experimental values of interplanar distances and intensities of diffraction peaks with the reference values.

The size and morphology of the powder particles were determined by transmission electron microscopy using an EMMA-4 (75 kV) microscope—microprobe. The samples were prepared by
deposition on the collodion support of the suspensions prepared by an UZDN-2T ultrasonic disperser and the subsequent deposition of carbon on it in a VUP-4 vacuum system.

3. Results of experiments and discussion

Photomicrographs of the deposit obtained by the electrochemical method showed that mainly two morphological types of cobalt precipitates—translucent amorphous measuring up to ~800 nm and lamellar 150—200 nm in size (Fig. 2a)—are represented in the structure of the deposit. It should be noted that the use of magnetic separation for separating metal particles from the stock solution leads to the appearance of remanent magnetization, under action of which the particles group together into larger clusters. Additional processing of the sediment in the RF discharge or mechanical or electrospark grinding of these aggregates was carried out to destroy them.

Figure 2. Photomicrographs of cobalt deposit (a) obtained by electrochemical method and (b) modified by RF plasma.

It was found that the resulting particles contain virtually no oxide phase, which is probably due to the coupled reaction of hydrogen release in the process of precipitation of the metals. Saturation with hydrogen of the electrolyte and sediment creates a reducing environment that allows synthesizing without an additional operation to remove oxygen from the solution.

A fine-grained structure prone to the formation of branched chains of particles 60-80 nm in size is formed after modification of nanosized cobalt by RF plasma (Fig. 2b). It can be assumed that the desorption of atoms and molecules of gases and liquids from the powder particles occurs during the evacuation prior to the initiation of RF discharge, which leads to release of active links on the surface and thus to restoration ability of the sorbent. Increasing the temperature and ion bombardment also contribute to desorption. Processing of nanoparticles in the plasma of an electric discharge in an atmosphere of inert gas reduces the surface energy of nanoparticles and decreases the size of their clusters (aggregates).

According to X-ray diffraction analysis, the main phase in the samples is pure cobalt in the form of a mixture of two crystalline polymorphic modifications—hexagonal α-Co and cubic β-Co. The diffraction pattern of a sample obtained by the electrochemical method is shown in Fig. 3. This diffraction pattern remains almost unchanged after the plasma modification of the high-frequency discharge, indicating no phase transformations. Reflexes 2.17, 2.04, 1.91, 1.254 and 1.069 Å agree with the hexagonal modification of cobalt, and 2.04, 1.78, 1.253, and 1.068 Å agree with the cubic modification (some reflections of these crystalline phases overlap). In addition, the reflex 2.44 Å, belonging to an unidentified phase, appears on the diffraction patterns of both samples.
Figure 3. Diffraction pattern of cobalt powder sample obtained by electrochemical method

The samples were a deformed sphere having on the surface a large number of spherical or needle-shaped nuclei forming a fractal structure with dimension $2 < D < 3$.

4. Conclusion
The ability to effectively disaggregate powders consisting of cobalt nanoparticles by the electrochemical method is shown. Plasma modification of Co powder in a RF gas discharge leads to ovalization and a decrease in particle size to 60-80 nm, the phase composition of the powder remaining essentially unchanged.

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