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Elaboration, characterization and magnetic properties of cobalt nanoparticles synthesized by ultrasonic spray pyrolysis followed by hydrogen reduction

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ABSTRACT

Nanostructured cobalt microspheres were synthesized by a two-stage method. First, cobalt oxide Co_3O_4 nanostructured microspheres were synthesized by spray pyrolysis at 700, 800, 900, 1000, and 1100, °C. Second, the nanostructured powders thus obtained were reduced to metal cobalt in a hydrogen atmosphere at 300 °C. For a sample obtained at 1000 °C, the influence of the reduction temperatures (220, 240, 270, 300, and 350 °C) on the metal cobalt powders properties was investigated. All the samples obtained were characterized by means of X-ray diffraction (XRD), coherent length determination and scanning electron microscopy (SEM). In addition, an average size of the particles, a specific surface area, and an effective diameter were determined. Finally, the magnetic properties of the metal cobalt, such as coercive force, saturation, and residual magnetization were measured by vibration sample magnetometer (VSM). The dependence on synthesis conditions of nanostructured metal cobalt microspheres properties was highlighted.

1. Introduction

Nanopowders and, more generally, nanostructured materials have led to many applications in various fields owing to remarkable electronic, magnetic, optical, and chemical properties of such materials. These properties strongly depend on size, structure, morphology, chemical composition for nanocompounds and hence on their methods of synthesis. Nanostructured magnetic materials deserve particular consideration. All of them are applied in storage devices, microwave absorption devices, ferrofluids, and different medical applications i.e., hyperthermia, drug delivery, medical diagnosis [1–5].

Among many transition metals and metal oxides, metal cobalt and cobalt oxides are important inorganic materials for a wide range of applications. Cobalt oxide Co_3O_4 is used as sensors, biosensors, lithium-ion batteries, and catalysis [6–8]. Depending on a synthesis method, Co_3O_4 exhibits different properties due to a wide range of morphologies, such as films, nanocubes, nanospheres, nanorods/nanowires, nanoplates/nanosheets, nanotubes, hollow structures, (meso)porous, nanochains, nanoporous walls and multi-shelled ones that were reviewed by Hussain [9] and Choi [10]. Cobalt nanoparticles are used in microwave adsorption devices [11–13], magnetic liquids for magnetic resonance tomography [14], and catalysis in the Fischer-Tropsh process [15–18]. Furthermore, nanostructured cobalt and its alloys are used as compounds in magnetic record devices [19,20], hyperthermia (cancer treatment) [21], etc.

For the synthesis of Co nanopowders the following approaches are commonly adopted: chemical precipitation, sol-gel route, plasma-chemical synthesis, and thermal decomposition of organic cobalt salts [22,23], chemical reduction [15,24,25], evaporation [26,27] and spray pyrolysis methods [23,28] and some other methods that were reviewed by Gubin and Koksharov [29] and Yılmaz [26]. Different methods and stages [15] of synthesis have an impact on the properties of nanosized cobalt. For instance, for cobalt nanopowders obtained by a wet chemical reduction reaction by Swain [15], the particle size ranging from 150 to 200 nm and a coercivity value of 522 Oe are observed. Cobalt nanopowders prepared by the same method with addition of surfactants [30] demonstrate the particle sizes of 9.2 nm and a

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coercivity of 425 Oe and 83 Oe for mole ratios of oleate/Co = 5 and acetate/Co = 40 respectively.

The use of spray pyrolysis methods for films deposition has been well-known since the 1980s [31]. Nowadays, spray pyrolysis is used for various applications.

The ultrasonic spray pyrolysis (USP) method allows to obtain nanopowders and nanostructured powders of metals [23], metal oxides [32–35], and composites [36,37]. The USP method was discussed in greater detail in [38] and [39]. The main advantages of the USP method are the simplicity of the equipment and the possibility to control composition and particle size through production conditions.

However, there is a lack of data on the dependence of the properties on the synthesis conditions in a particular case of nanostructured cobalt powders obtained by the USP method and followed by hydrogen reduction.

This study aims to define optimum conditions for the synthesis process of nanostructured cobalt microspheres by means of a two-stage method. This method comprises the synthesis of Co_3O_4 nanostructured microspheres by a USP method and the subsequent reduction to metal cobalt in a hydrogen atmosphere. The method allows controlling the properties of nanostructured cobalt microspheres, such as composition, structure, morphology, and magnetic properties.

2. Experimental

2.1. Materials and methods

2.1.1. Materials used

The solution (10 wt.%) of analytical grade cobalt nitrate salt $Co(NO_3)_2 \times 6H_2O$ (Labteh, Russia) in distilled water was used as a precursor. To prepare 5 L of solution, 790 g of $Co(NO_3)_2 \times 6H_2O$ was dissolved in 4180 mL of distilled water in order to obtain 160 g of Co nanopowder.

2.1.2. Synthesis of cobalt nanostructured powders

2.1.2.1. Co_3O_4 microspheres synthesis. Fig. 1 presents a schematic view of the USP apparatus used in the present work. The high frequency ultrasonic generators (1) were placed in a container of the Co nitrate solution (2). The frequency of the generators was in the range from 1.7 to 2.2 MHz. The aerosol was pumped with Vacuubrand MZ 2C NT + AK + EK (8) into a quartz tubular reactor (4) heated by an electrical furnace Nabertherm RT 50/250/13 (3) to 700, 800, 900, 1000 or 1100 °C. Heating of the aerosol resulted in the evaporation of water and the decomposition of the salt solution droplets into cobalt oxide Co_3O_4.

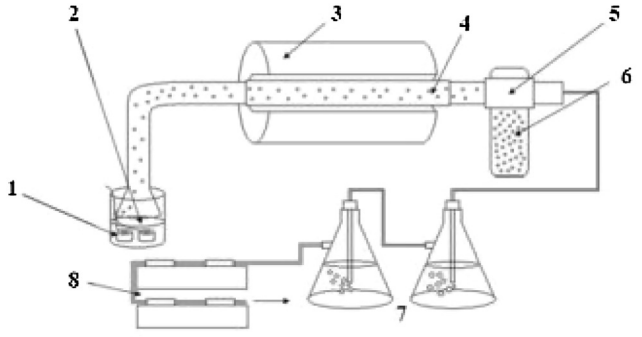

Fig. 1. Schematic drawing of the ultrasonic spray pyrolysis apparatus used for the synthesis of Co_3O_4 nanostructured microspheres. The various elements are labeled: (1) high frequency ultrasonic generators, (2) container of the Co nitrate solution, (3) electrical furnace, (4) quartz tubular reactor, (5) filter, (6) powder container, (7) container for the solution and (8) vacuum pump.

The obtained aerosol was passed through a filter (5) to collect a powder (6). The alkali solution (7) was used to neutralize of the waste gaseous medium.

The process of microspheres formation in this apparatus was discussed previously in great detail in our paper [40]. In brief, the aerosol generator produced droplets with the average diameter at the range from 0.5 to 10 μm. The aerosol moved into the reactor, where the droplets evaporated and thermally decomposed into a metal oxide that inherited the droplets shape [41,42].

Pyrolysis temperature depends on the equipment features [38]. For the samples obtained below some temperature the heat flow is deficient to water evaporation process and the samples are too moisture and have tendency to agglomerate in the filter. That is why, in our research, we chose pyrolysis temperatures above 700 °C. For instance, accordingly to TGA data Co_3O_4 obtained at 700 °C contained 14.3% of water, whereas Co_3O_4 obtained at 1100 °C contained 4.51%.

2.1.2.2. Co nanostructured powders synthesis

2.1.2.2.1. Method used to investigate the influence of the pyrolysis temperature on the metal cobalt properties. The obtained nanostructured Co_3O_4 powder was reduced to metal cobalt by a thermal treatment in the furnace Carbolite HZS 12/600E at 300 °C under a continuous flow of hydrogen. The heating sequence was as follows. First, increasing the temperature at a rate of 20°/min up to 200 °C and maintaining this temperature for 20 min. Then, with a heat rate of 15°/min up to 250 °C and, again, maintaining this temperature during 20 min. Finally, with a heat rate of 5°/min up to 300 °C and maintaining this temperature. After 60 min the furnace was allowed to cool down.

2.1.2.2.2. Method used to investigate the influence of the reduction temperature on the metal cobalt properties. To investigate the influence of the reduction temperature on the properties of the nanostructured cobalt oxide, a sample pyrolysed at 1000 °C was selected. This pyrolysis temperature corresponds to the optimum value of the Gibbs energy for the decomposition reaction of cobalt nitrate [23].

The reduction temperatures were 220, 240, 250, 270, 300, and 350 °C.

All the reduced metallic cobalt particles were passivated under nitrogen atmosphere of technical purity.

2.1.3. Characterization

The phase structure was determined by a method of the X-ray phase analysis on a Difrey 401 (Cr, λ = 0.229 nm) x-ray diffractometer with Bregga-Bretano focusing. The average size of the coherent-scattering region was calculated by the diffraction profiles broadenings.

The morphology, dispersion and elemental composition of the samples were studied by a JEOL JSM-6610LV scanning electron microscope (SEM). In addition, thermogravimetric analyses were carried out by a TGA SDT Q600. Specific surface areas were measured by means of an Accusorb 2100E, whereas the particle size distributions were measured using a Fritsch Analysette-22 Nanotech.

Room temperature magnetic properties were investigated by the VSM Lake Shore-7407 vibration magnetometer in magnetic fields up to 10 kOe. Cobalt nanopowder samples were placed in flat plastic capsules that were fixed on a holder of the magnetometer. Nickel standard weighing 7 mg ($0.385 \cdot 10^{-4}$ T of cm^3) was used to calibrate the system (the absolute value of the magnetic moment). Two series of measurements of the magnetic properties for each sample were carried out. The values of the coercive force and the