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Production of cobalt nanopowders by electron-beam technology and their NMR and magnetometry study

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ABSTRACT

Complex structure, magnetometry and NMR investigation of nanostructural cobalt powders synthesized using electron-beam technology was carried out. The developed technology makes it possible to fabricate roentgen-amorphous nanosized cobalt powders containing highly anisotropic HCP phase which does not require additional passivation measures. Magnetometry and NMR data are in correspondence with the results of structure measurements.

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1. Introduction

Magnetic nanoparticles (MNP) and their composites on the basis of homogeneous diamagnetic matrix are perspective materials for practical applications [1].

Magnetic properties of MNP are defined mainly by their chemical composition, crystal lattice type and degree of its defectivity, size and shape of MNP, their interaction with surrounding matrix and neighbor MNPs. Changing mean sizes of MNPs, their size distribution functions, degree of matrix space filling, phase composition of magnetic inclusion and surrounding them by a diamagnetic medium, it is possible to vary in a wide range magnetic properties of materials synthesized on their basis. New technologies are currently actively developed with an aim to develop of new composite materials with their magnetic properties and structure under control. For this aim it is more suitable to use nanomaterials with better controllable properties and larger specific magnetization, such as Co, Fe, Ni and their alloys. Up to now the main biomedical applications were related with iron oxides the synthesis of which is less subject to control.

It is known that memory systems with a high density recording capacity are in need of magnetic nanostructures materials with high magnetocrystalline anisotropy, such as hexagonal close packed (HCP) Co, and less anisotropic face-centered cubic (FCC) phases are more applicable in biomedicine (hyperthermia) applications [2]. Therefore, the great interest is related to the development of new effective methods for synthesis of cobalt nanopowder with controllable anisotropy and composites based on them.

As it is known [1], there are the following main approaches to nanoparticle synthesis: fabrication from macroscopic materials by dispersion and methods of chemical synthesis related with the controlled change of material composition with stopping of new phase growth at nanosize stage.

The methods of MNP fabrication in gas or solid matrix using high-energy influences on materials are considered as physical, and methods of their synthesis in solutions are attributed to chemical ones.

In work [3] the conditions of fabrication of highly anisotropic HCP cobalt phase using the sputtering technique were studied. The close relation between the particle size and its crystallographic phase was established. It turned out that HCP phase is characteristic for mean diameter (D) particles, $D \geq 40$ nm, while for particles with D $\sim$30 nm a mixture of HCP and FCC was observed and under 20 nm the pure HCP phase was characterized with comparatively small anisotropy.

In work [4] the HCP Co nanoparticles with D$\sim$2 nm were synthesized using the silica matrix based ion implantation technology.

In the current work we study the magnetic and structural properties of cobalt MNP, synthesized using the electron-beam

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technology and their composites on the basis of silicon polymer matrix. Investigations of structural characteristics of MNPs were carried out using X-ray diffraction and Auger electronic spectroscopy methods.

Magnetic measurements were performed using methods of vibration sample magnetometry (VSM) and NMR. These methods are complementary to each other, as the magnetometry is attributed to the macroscopic measurement methods while NMR is a powerful microscopic method. So, in work [5] an example of a coarse-grained nanocomposite on the of basis of cobalt nanoparticles, it was shown that with the help of ^{59}Co NMR one could unambiguously define what crystal structure, cubic or hexagonal, is realized in cobalt nanopowders that could not be made unambiguously using the standard roentgen-analysis method.

2. Experimental results and discussions

In this work for synthesis of nanosized cobalt and other metal powders the electron beam technology is used which according to the above introduced classification belongs to the physical methods. The process envisages the evaporation of starting material (1, Fig. 1) by electron (2) from a water-cooled copper crucible (3) and the following condensation of vapor stream (4) on the substrate surface (condenser, 5) supercooled to a proper temperature. The technology process proceeds in vacuum ($\sim 5 \times 10^{-2}$ Pa).

The electron-beam technology developed by us for production of nanocrystalline powders makes it possible to avoid many problems and shortages inherent in currently existing process. The focused electron beam enables to evaporate most of the refractory elements and chemical compounds excluding essentially the necessity of materials choice in respect to the melting or evaporation temperatures. The application of water-cooled copper crucibles and the carrying out of the process under vacuum ensure a high purity of vapor stream and, as a result, of the final product.

The process excludes the necessity of the previous treatment of starting materials. The phase content and grain size of the condensed phase is mainly influenced by the temperature, surface cleanness and substrate material. The electron-beam technology makes it possible to condense the vapor stream with enormous thermal energy on substrates made of any materials in a wide range of temperatures – from cryogenic to higher ones. This provides the considerable overcooling and oversaturation of vapor stream which is one of the necessary conditions for formation of nanocrystalline structure materials [6].

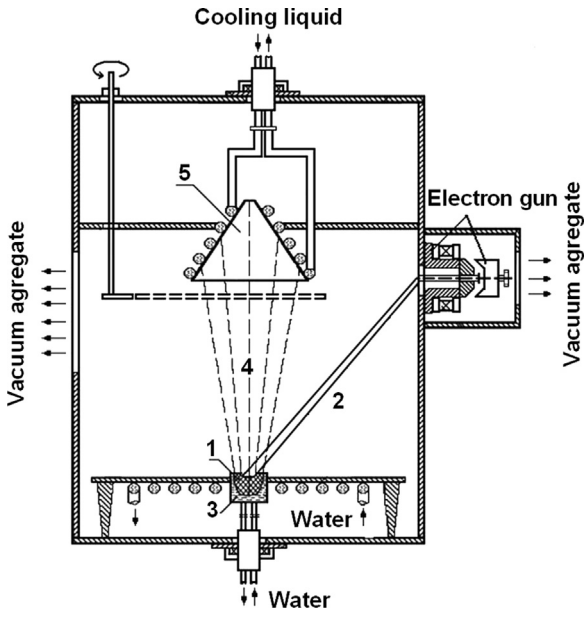

Fig. 1. Setup for cobalt nanopowder production process: (1) starting material, (2) electron beam, (3) water-cooled copper crucible, (4) vapor stream and (5) substrate (condenser).

The morphology and phase content study of cobalt powders was carried out by scanning electron microscope DSM-960 (OPTON, Germany), supplied with the Roentgen microanalyzer, the Auger-electron spectrometer LAS-2000 (RIBER, France) and X-ray diffractometer HZG-4/A-2.

The metallography analysis clearly reveals the inhomogeneities of microstructure of condensate particles – along with arbitrarily scattered, rather ultra-dispersed particles are clearly seen large, close to the spheroidal shape aggregates. The formation of such aggregations points to the unification of particles, close by orientations, in one aggregate (conglomerate).

Allowing for the fact that vapor stream absorption of the substrate proceeds with the thermal accommodation, and at the formation of metallic films the processes of surface migration are not observed below 200 °C [7], one could suppose that conglomerates are formed in the vapor phase and their fixing on the condenser surface is realized on the subsequent stage of the process. But the arbitrary scattered nanoparticles are the result of direct constitution of the vapor stream.

Therefore, the slowing down of the self-diffusion processes of atoms, precipitated on the overcooled substrate, creates the conditions for obtaining separate highly dispersed particles as result of collisions of ultradispersed fragments of vapor stream with the substrate.

The X-ray diffraction analysis data speak on nanosize, roentgen-amorphous structure of synthesized metal grains (c, Fig. 2).

Auger-spectroscopy investigation of cobalt powders was also carried out (pressed in tin tablets) [8]. Fig. 3 presents the Auger-spectra of Co surface before the beginning of bombardment by argon ions (a) and after the removal of layers with thicknesses ~200 (b), 400 (c) and 600 (d) Å. As it follows from Fig. 3a, the spectrum consists of small intensity cobalt and carbon peaks, and the intensive peak of oxygen $KL_{2,3}L_{2,3}$ Auger-transitions. The fine structure of oxygen $KL_{2,3}L_{2,3}$ Auger-transitions before the beginning of bombardment using argon ions, and also correlation between the intensities of the corresponding peaks of cobalt LMM Auger-transition, indicate that oxygen is not in chemical bonding with the metal atoms and adsorbed layer on the surface of the sample (consisting mainly of oxygen) is in the state of physical adsorption.

Fine structures of the peaks composing the spectrum did not practically change in the process of the removal of the layer ~200–600 Å in thickness from the reference surface of the sample. However, the decrease of intensity of the oxygen peak was noticed, while intensites of triplet peaks of LMM Auger-transition of cobalt atoms were increased (Fig. 3, a–d) and nearing the calculated value of the peaks for the free cobalt atoms.

Consequently, adsorbed layer on the surface of the nanoparticles of cobalt powder (before compacting) was in the state of physical adsorption and did not take part in the oxidizing of the cobalt atoms. The effective thickness of this layer did not exceed ~60 Å. For this reason, nanosized Co powder, produced by us through evaporation by means of electron beam and followed condensation of the vapor steam in vacuum, does not need the additional passivation.

Along with structure and chemical characterization of samples, the essential significance are data on their magnetic properties, because they define the most interesting practical applications of magnetic nanostructures.

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