Volume 6, Issue 3, 2016, 1276-1279 **ISSN 2069-5837**

Biointerface Research in Applied Chemistry

www.BiointerfaceResearch.com

Original Research Article **Open Access Journal**

Received: 18.03.2016 / Revised: 22.05.2016 / Accepted: 28.05.2016 / Published on-line: 15.06.2016

Synthesis and some properties of nanostructured Ni-Co alloys

Kagakin Evgeniy I.[1], Lapsina Polina V. [2], Popova Anna N. [2,*], Dodonov Vadim G.[3]

[1]Kuzbass State Technical University, 28, Vesennyaya str., Kemerovo, 650000, Russia
[2]The Federal Research Centre of Coal and Coal Chemistry of Siberian Branch of the Russian Academy of Sciences, Russia
[3]Kemerovo State University, 6, Krasnaya str., Kemerovo, 650000, Russia

*corresponding author e-mail address:***h991@yandex.ru***

ABSTRACT

In the paper, synthesis and some features of Ni-Co nanopowders were studied. Nanoparticles were prepared by reducing mix of sparingly soluble nickel and cobalt carbonates with hydrazine hydrate as the reducing agent. The morphologies and the crystalline structures of the products were characterized by using scanning electron microscopy (SEM), and atomic force microscopy (AFM) and powder X-ray diffraction (XRD). In particular, formation of solid solution was defined for Ni-Co systems obtained by proposed a method. The steady-state crystallites size of the binary systems were of the 15-20 nm.

Keywords: *nanostructured powders, nickel, cobalt, hydrazine hydrate, poorly soluble salt.*

1. INTRODUCTION

Nanostructured materials, which are include the nanoparticles or the nanolayers of ferromagnetic metals and alloys in own structure, have attracted extensive interest in recent year because of their fundamentals properties and wide range of applications. Cobalt and nickel-based alloys are particularly attractive because of their magnetic properties, high saturation magnetization, low coercivity, high magnetic permeability and high Curie temperature [1, 2]. An important application field for Co and Ni nanoparticles is biotechnology. In the field of nanobiotechnology, magnetic nanoparticles can be used for cancer therapy, cellular separation, and medical imaging [3 – 5]. Private interest is the nanoparticles of alloys of the Ni-Co, whose properties are often superior to those of metals and their constituents. Such materials can be used in the systems of magnetic recording [6], the high-frequency devices [7, 8], and the systems of protection from electromagnetic radiation [9] in the range of 4-18 GHz.Catalyticapplications for Co and Ni nanoparticles include, for example, hydrogenation, oxygen reduction, water splitting, and synthesis of higher alcohols [10 – 13]. In these applications, nanoparticles offer high specific surface areas and easier dispersion compared to catalysts with larger dimensions.

At the same time, methods of synthesis and, especially, properties of the Ni-Co nanosystems have hardly been studied systematically nowadays. Moreover, from the fundamental point of view it is very important to define possibility of Ni-Co synthesis by reduction of sparingly soluble salts.

2. EXPERIMENTAL SECTION

Nanocrystalline Co-Ni alloys were prepared by a chemical process involving the reduction of a mixture of sparingly soluble nickel and cobalt carbonates at 80 ºC with hydrazine hydrate as the reducing agent. Obtained gray solid particles were filtered, washed first with distilled water several times and finally with isopropyl alcohol to remove hydrazine and allowed to dry at room temperature. The sample was kept in glass-stoppered bottle.

Microstructural evaluation was studied with Scanning Electron Microscopy (SEM) of JEOL model JSM-6390 and Atomic Force Microscopy (AFM) (Cypher™ Atomic Force Microscope, Asylum Research), elemental composition – by x-ray fluorescence analysis with an energy dispersive X-ray (EDX) analyzer (in conjunction with SEM). The samples' structure was characterized by X-ray powder diffraction (XRD) using a BRUKER D8-Advance X-ray diffractometer (Fe-Kα radiation, λ=0.193604 nm) to identify the nanocrystalline state of the alloys and the phase of the crystalline grains. The XRD study was carried out at 2Θ angle range of 20°-140°, angular step is 0.02°. XRD patterns were processed using Diffrac.Suite.Eva (V3.1) software platform. ICDD PDF-2 database was used for decoding of diffraction patterns. To calculate the crystallite size the Scherrer Formula: $D=\lambda/\beta\cdot\cos\theta$ (λ - the radiation wavelength, θ - angle of diffraction reflection, β - broadening of the diffraction lines in diffraction patterns (in the scale of 2θ)) was used. The functions of particles distribution on size were calculated from curves obtained by the method of small-angle X-ray scattering (SAXS) at characteristic Fe-emission with impulses count at angles region 2θ from 0.05° to 3°.

3. RESULTS SECTION

Numerous techniques have been developed to prepare bimetallic nanosystems by ions reduction [14 – 22]; among them, direct reducing method using metal salt solutions with hydrazine hydrate, and the electrochemical deposition of alloys. However,

there is no complex research of the effect of synthesis conditions on size and shape characteristics of Ni-Co nanostructured powders reduced from sparingly soluble salts.

In this work, we reported on synthesis of Ni-Co alloys nanoparticles by reduction of mix of sparingly soluble nickel and cobalt carbonates with hydrazine hydrate as the reducing agent [23].

It is found that Ni100-xCox nanosystems prepared from a mixture of sparingly soluble salts with hydrazine hydrate by the proposed chemical reduction method are, obviously, nanostructured solid solutions, as evidence of the X-ray diffraction patterns (Figure 1).

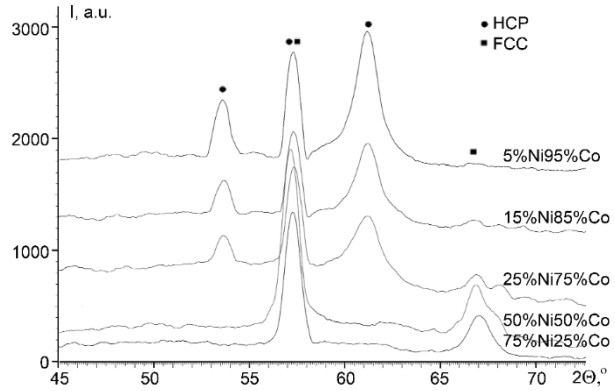

Figure 1. XRD-pattern of nanostructured Ni-Co powders

It is shown by XRD-method (Figure 2) that the coreduction of the mixtures of nickel and cobalt carbonates with hydrazine hydrate conduces to formation of either individual or co-existing two metal phases (hexagonal close-packed (HCP) and face-centered cubic (FCC)), depending on the mixtures composition. Reduction of the mixtures with 0–20% nickel gives the HCP-phase. Values of the unit cell volume (UCV) and the average atomic volume (AAV) are slightly decreased with approximately linear relationship when nickel content is increased. FCC-phase is formed when nickel content is more than 25%, it coexists with HCP-phase, the content of the last one is decreased up to total disappearance when nickel content is 50%.

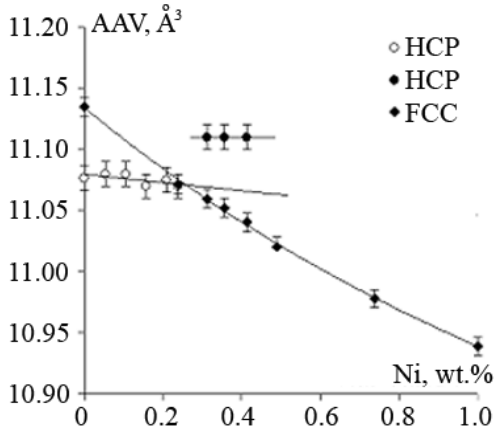

Figure 2. The average atomic volume (AAV) dependence of the system composition for Ni-Co nanopowders

The relatively small amount of the HCP-phase in the compositions of 30-40% Ni allows to measure the lattice parameter and AAV of FCC-phase with good accuracy. In contrast, the presence of large amounts of the FCC-phase prevents to measure parameters of HCP-phase, however, it should be recognize validity of abnormally high values of AAV of HCP-phase (as the unit cell volume). Apparently, in this contain area there is a supersaturated solid solution with the metal nickel HCP-phase, so an abnormal increase of the AAV is the result of a specific effect of excessive nickel amounts on the structure.

On the one hand, the single phase area in the compositions of 0-20% Ni well corresponds to one type of the phase diagram [24]. On the other, two phase area in a wide range of 25-50% Ni is similar to [25], but in this case for the two-phase area it would not have to change the lattice parameter of the FCC-phase. Therefore, the complexity of the phase state of the nanostructured system is not directly correlated with the phase diagram.

The average size of nanocrystallites Ni-Co powders is estimated by the Scherrer method (the broadening diffraction peak at half-maximum). The crystallite sizes for the obtaining binary systems are of the 15-20 nm.

The results obtained by SEM have shown that the Ni-Co systems are mainly spherically shaped particles with size up to several microns, comprising of nanoscale structures, regardless of the system composition (Figure 3). The data obtained by small angle X-ray scattering (SAXS) have shown that the distribution functions of the particle size have multimodal type (Figure 4).

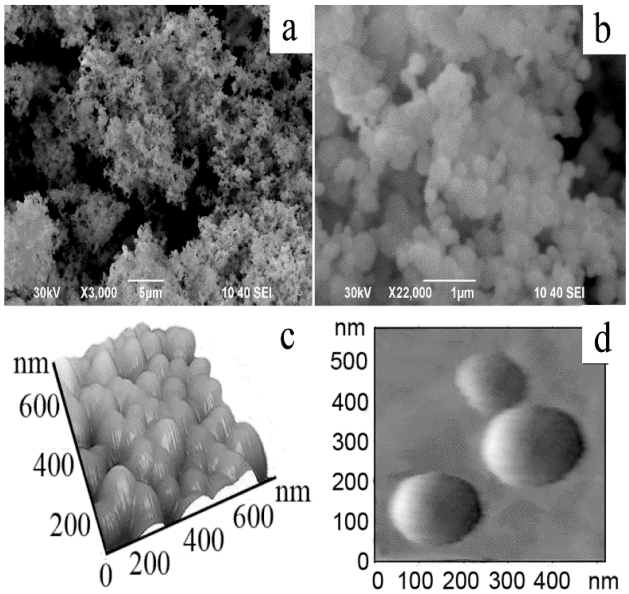

Figure 3. SEM (a, b) and AFM (c, d,) image of Ni-Co systems: a) Ni/Co 0.25/0.75; b) Ni/Co 0.5/0.5

However, there are two main modes. The first peak, located in the region of up to 50 nm (Figure 4), refers to the nanocrystallites, which are composed of agglomerates.

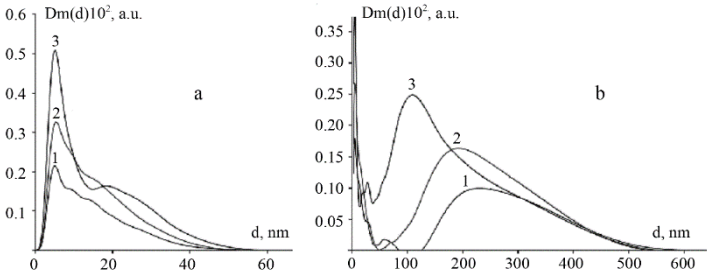

Figure 4. Mass-functions of particles size distribution calculated by SAXS for Ni-Co systems (1 − Ni/Co 0.25/0.75; 2 − Ni/Co 0.5/0.5; 3 − Ni/Co 0.75/0.25)

The second maximum is in the region of 0.1-0.6 microns; it has aggregative nature and characterizes the size of the original nanocrystallites agglomerates (Figure 4b). With the increasing proportion of nickel in the system, the intensity distribution function significantly is increased simultaneously; and, withal, maximum of agglomerates is shifted significantly to smaller sizes. This may be due to the fact that having more value of solubility product (Ksp ($NiCO_3$) ~ 10-7, Ksp($CoCO_3$) ~ 10-13), nickel carbonate provides a large number of nucleation sites, thereby, it is forming a greater amount of nanocrystallites.

Data analysis of the elemental composition has shown that the nickel content in the obtained system is slightly reduced in comparison with the predetermined components ratio. This may be due to the different solubility of the components. Another possible reason could be that the composition of the obtained carbonates, which used as precursors, is undefined. Carbonates of nickel and cobalt are precipitated from the metal chloride solutions by sodium carbonate; at the same, it is likely to be formed hydroxycarbonates. It has not taken into account for the systems preparation. The data defined by XRF have shown that the oxygen content in the resulting system is in the range of 8-25 wt. %.

Based on the results obtained by the complex of different methods, morphology of the Ni-Co systems is characterized by a multi-level hierarchy. The smallest fraction is presented by nanocrystallites which size is 15-20 nm. Nanocrystallites are composed into aggregates of the 1st level, with dimensions of 100-400 nm. These aggregates in turn form larger associates of the 2nd level of spherical shape mainly. As for systems with a lower nickel content (less than 50 wt.%), the associates can be merged into associates of the 3rd level.

4. CONCLUSIONS

It is shown the possibility of synthesis of the nanoscale Ni-Co systems by the reduction of the mixtures of sparingly soluble metal salts with aqueous solutions of hydrazine hydrate. It is suggested that morphology of the nanoscale Ni-Co systems is multi-level.

This method of synthesis is notable for several advantages: availability of precursors and equipment performance of synthesis, low power consumption, obtaining the necessary amount of the product without impurities.

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6. ACKNOWLEDGEMENTS

Authors would like to thank Dr. V.M. Pugachev, we are indebted to him for his insight to the project as well as endless discussions. Assistance by Sergey Lyrshchikov for microscope experiments is gratefully acknowledged.

This work was supported by Russian Foundation for Basic Research (RFBR project 16-33-00829_mol_a).

This work was carried out in a center of shared usage of equipment of The Federal Research Center of Coal and Coal Chemistry of Siberian Branch of the Russian Academy of Sciences (FRC CCC SB RAS) and Kemerovo State University.