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Influence of the Ratio of Metal Composed Nanocomposites Fe-Co / C on Phase Composition

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It is found that the chemical composition of the metal component of nanocomposites satisfies the Fe: Co ratio, that was set on at the stage of preparation of the precursor, wherein there is a slight deviation from the initial metal concentration, due, apparently, to removing metal from the nanocomposite by the formation of volatile carbonyls of iron and cobalt in IR heating.

Keywords: Metal-carbon nanocomposites, Nanoparticles FeCo, IR-pyrolisis, PAN.

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1. INTRODUCTION

Significant interest in nano-structured material for this including in the structure of ferromagnetic nanoparticles of metals and alloys caused by specific magnetic properties, manifested in the nano state: high magnetization and coercivity, the lower the Curie temperature, high anisotropy, etc. These materials may find use in magnetic recording systems, high frequency devices MRI and Biomedicine, protection systems electromagnetic radiation. [1]. Additional ferromagnetic alloys FeCo-allocated nanoscale structures as have one of the highest values of magnetization, wherein the magnetic properties are strongly dependent on the composition and dispersion of the alloy. A number of studies [2, 3] demonstrated the effectiveness of the use of nanoparticles in FeCo absorbers of electromagnetic waves in the range of 4-18 GHz. There are several different approaches to the synthesis of nanoparticles FeCo. Features of methods is the most significant quantity of the synthetic steps, the need for stabilization using surfactants, additional recovery step in a hydrogen atmosphere, a significant duration processes. One solution is the inclusion of nanoparticles in the composites [4-5]. This allows controlling the size of the nanoparticles improve chemical stability, reduce the density and weight of the composite coating.

The developed methodology allows us to synthesize FeCo nanoparticles composed of metal-carbon nanocomposites in one step by the IR - heating, ie in the same process at the same time forming a carbon nanocomposite and nanostructured matrix is the formation of alloy nanoparticles FeCo.

2. EXPERIMENTAL SECTION

Polyacrylonitrile (PAN) was synthesized in the presence of a redox catalyst system. Film precursor composition was obtained from the combined solution in DMF (Fluka, 99.5 %) of PAS, iron acetylacetonate hydrate (III) (Acros Organics, 99 %) or ferrocene (Acros Organics, 99 %) and cobalt acetate (II) (Acros Organics, 99 %) followed by removal of solvent at $T \leq 70$ °C. The concentration of PAN in DMF solution was 5 wt. %. The total concentration of metals in the precursor 20 wt. % by weight of PAN metal ratio Fe: Co = 1:1, 1:3, 3:1, by weight. Pyrolysis was carried out in a laboratory furnace of IR-heating [6]. The precursors was heated at 150 and 200 °C for 15 min. at each temperature. This processing is necessary to remove the solvent bound with the polymer and the initialisation of process structuring of PAN. The samples were heated to the desired temperature of the main infrared pyrolysis process, which was 300-800 °C, the time exposure at the required temperature of infrared heating time was 2-10 min. The process was carried out in vacuum ($P \sim 10^{-2}$-10^{-3} mm Hg).

X-ray diffraction analysis was performed on the X-ray powder diffractometer EMMA, equipped with a high voltage generator type IGBT, midrange output of 3 kW (60 kV / 80 mA) with high stability of ± 0.005 %. In most diffractometer uses standard Proven anode X-ray tube (anti-cathode) of copper with low power 2.2 kW. Focal spot size – 0.4 × 12 mm. As a device for recording the scattered X-radiation detector is used Xe proportional detector for focusing geometry with a graphite monochromator. Reflexes are recorded using a goniometer radius of 180-250 mm with a range of changes 2θ: – 30-160° with a minimum step on each axis – 0.002. Software VisualXRD, Traces v.6, Siroquant provides automated control at all stages of the measurements. In addition, there is an automated database containing 250,000 records for the automatic identification of the diffraction patterns obtained, it is even more facilitated the implementation of the totality of the planned research.

The surface morphology and composition of the samples were determined using a scanning electron microscope (SEM) JEOL JSM6610LV (W-cathode). Detectors of secondary and backscattered electrons can allow to register the signals in the different mods: composite, topographical and shadow contrasts; the energy dispersive analyzer (X-Max Silicon Drift Detector Oxford Instruments) is used for elemental analysis of the surface layer. Two modes: high and low vacuum SEM, the application of conductive films of platinum (JEOL

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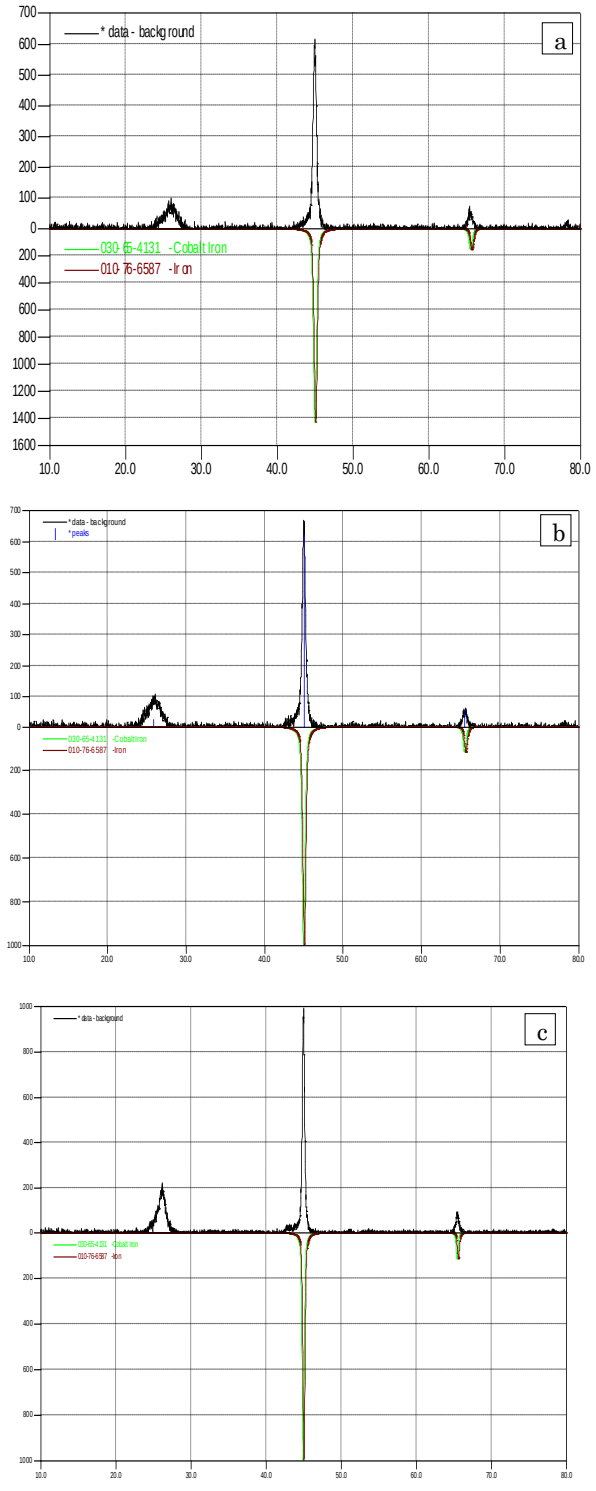

Fig. 1 – X-ray analysis of nanocomposite FeCo / C (Fe:Co = 1:1), synthesized at differents temperatures: 600 °C (a), 700 °C (b), 800 °C (c)

JFC- 1600 Auto Fine Coater) can acquire images at an accelerating voltage of 300 V to 30 kV magnification range 5÷300,000 times the spatial increase to 3 nm regardless of sample conductivity.

Metal-carbon nanocomposites were prepared based on polyacrylonitrile (PAN) and the compounds of Fe and Co. By results of X-ray analysis it was established that nanocomposites are homogeneous material, wherein the nanoparticle metal (Fe, Co) or FeCo-alloys are distributed in the graphitelike carbon matrix. Fig. 1 shows the result of X-ray analysis of nanocomposites obtained at T = 600-800 °C (Fe: Co = 1:1).

Amorphous halo, which characteristic for weakly ordered carbon structures, is fixed on the of all the samples in the range of angles 20°-30°. The amorphous halo on X-ray diffraction patterns is associated with irregular displacement of graphene planes relative to each other and the small size of the coherent dispersion of crystallite of graphitelike phase [6]. During process of IR-pyrolysis of polymer are secreted significant amounts of various gaseous products (H_2, NH_3, CO etc.), which can recover metal from their compounds [7]. It should be noted that the recovery takes place in the solid polymer phase, so that the recovery of the metal occurs in situ, where atomic hydrogen which is generated due to degradation of the polymer backbone during the IR heating can participate in the recovery process.

The diffractograms of nanocomposites, synthesized at temperatures 600-800 °C, is contain several maxima (45; 65,5°) corresponding to angles of reflection from the FeCo phase in the range of scattering angles 2θ from 50° to 80°. Reflexes phase fcc-Co is very weak at large angles, which also confirms the formation of the alloy FeCo, having the bcc lattice. The intensity of these reflections is increased, which indicates an increase in the size of alloy nanoparticles with increasing temperature synthesis of nanocomposites. Simultaneously, there is an increase in the intensity of the halo (2θ from 20° to 30°) and the displacement of its maximum in the region of large angles, which is associated with the processes of graphitization and the formation of graphitelike structure with a larger size of crystallites.

When used other ratio of metal-containing components (Fe: Co = 1:3) for the synthesis of nanocomposites, the material, having a different composition of the phases, are formed. On the diffraction patterns for samples, synthesized for T = 600-800 °C, along with the phase of the alloy FeCo the reflexes of phase fcc-cobalt are clearly recorded (2θ = 44, 51.3). Fig. 2 shows XRD-pattern nanocomposite FeCo / C (Fe: Co = 1:3), synthesized at T = 800 C.

Apparently, the formation of intermetallic nanoparticles occurs in several stages: first, there is a restoration of cobalt acetate and nanoparticles are formed. Then the iron is reduced and reacted with nanoparticles Co, dissolved in they. In result, solid solution of Fe

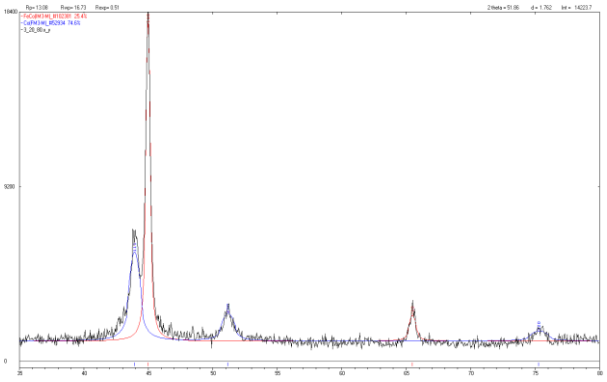

Fig. 2 – X-ray analysis of nanocomposite FeCo / C (Fe : Co = 1:3), synthesized at T = 700 °C

in Co is formed. This is supported by the fact that according to the thermodynamics, the temperature of reduce of cobalt compounds by hydrogen is substantially lower (~ 200 °C), than for iron (~ 400 °C). Because of an excess content of cobalt the nanoparticles are formed to fcc-phase, which do not react with iron or solid solution Fe in Co is formed in with concentration less than 10 %, which also has an fcc-lattice.

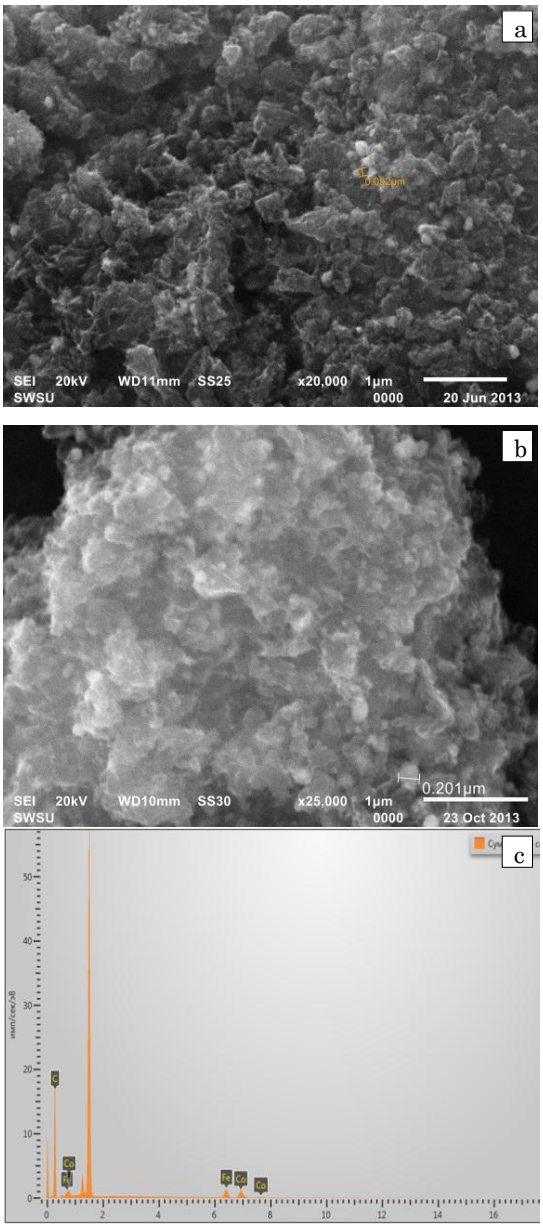

Fig. 3 – SEM nanocomposite FeCo / C synthesized at $T = 700$ °C (a) and 800 °C (b), and the results of energy-dispersive analysis (c)

Table 1 – The results of the chemical analysis of nanocomposites FeCo / C

Ratio Fe:Co	Temperature of synthesis, °C	Content, wt.%		
		C	Fe	Co
1:1	600	82,3	8,4	9,3
	700	82,7	7,9	9,3
	800	82,3	8,6	9,1
1:3	600	83,9	3,8	12,3
	800	79,9	4,7	15,4

The results of the SEM with using the console of X-ray dispersion chemical analysis are supports this assumption, because the ratio Fe:Co is remains practically unchanged in all samples and corresponds to the original, i.e. the loss of metals during the IR processing of the precursor are comparable. SEM results of nanocomposite FeCo/C (1:1), obtained at $T = 800$ °C, are shown in Fig. 3.

The summarized results of the chemical analysis of nanocomposites of Fe: Co = 1:1 and 1:3 were obtained under different conditions are presented Table 1.

For all samples, the ratio of Fe: Co slightly different from the original. Differences may be due to the difference in temperature of reduce of the metal. Also, a slight reduction of the total concentration of the metal observed with increasing temperature synthesis of nanocomposites. apparently, during the synthesis process volatile carbonyls of iron and cobalt are formed, which are released into a gas phase and pumped by a vacuum system of IR heating apparatus. As a result, a metal-carbon nanocomposite are formed, where in the metal content by a few percent lower than the original. After forming the metal nanoparticles or alloy this process has little effect on the chemical composition of the resulting material.

3. CONCLUSIONS

Nanoparticles of alloy of FeCo were obtained in the metal-carbon nanocomposites based on polyacrylonitrile under IR - heating. It was found that the initial ratio of metal introduced into the precursor affects the phase composition of the nanocomposite. It is shown that increasing the temperature of synthesis result increases the size of FeCo alloy nanoparticles, thus there increases the size of the crystallites of the graphitelike matrix of nanocomposites. Chemical composition of the nanocomposite weakly dependent on synthesis temperature and determined by the initial metal ratio.

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