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The Influence of Synthesis Temperature on the Structure, Composition and Magnetic Properties of Nanocomposites NiCo/C

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By method of IR-pyrolysis the precursor of polyacrylonitrile and compounds of cobalt and nickel metal-carbon nanocomposites were obtained, representing nanoparticles of alloy NiCo, dispersed in nanocrystalline carbon matrix. NiCo / C nanocomposites are ferromagnets. Magnetization and the coercive force depends on the size and composition of the alloy nanoparticles NiCo. The average size of metal nanoparticles is determined by the synthesis temperature and in range of 350-800 °C is 10-80 nm, respectively. According to the results of TEM it was detected that with increasing synthesis temperature the maximum synthesis of nanoparticles size distribution shifts to larger sizes. The magnetization and coercivity depend on the size and composition of the nanoparticles of alloy NiCo. With increasing synthesis temperature from 350 to 800 °C the magnetization increases from 0.055 to 17 A·m²/kg.

Keywords: Metal-carbon nanocomposites, Nanoparticles NiCo, Magnetic properties of nanoparticles, IR-heating.

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1. INTRODUCTION

The interest in metal-carbon nanocomposites is associated with the prospect of their application as magnetic materials. One of the areas of application of these materials is their use as absorbers of electromagnetic radiation [1]. Thanks to the synergy of the electromagnetic properties of metal nanoparticles and a carbon matrix, metal-carbon nanocomposites are capable of absorbing a large portion of incident electromagnetic radiation [2]. Methods for the synthesis of metal-carbon nanocomposites using IR-heating are proposed in the literature [3-5]. Thus obtained material are the dispersion of nanoparticle Ni or NiCo in the carbon matrix.

The study of the characteristics of nanocomposites synthesized at different concentrations and modes of synthesis is promising. The possibility of synthesis of nanoparticles NiCo alloy in carbon matrix was shown in the work [4], and magnetic properties of nanocomposites NiCo / C with the initial composition of metals in the precursor 1 : 1, obtained at different temperatures were characterized. Due to the fact that on the phase diagram of Ni-Co for bulk materials [6] in the range of concentrations of Nickel from 0 to 55 at. % possible formation α and ε of cobalt, the study of nanoparticles Ni-Co alloy with a large volume of the Co content is interesting.

2. EXPERIMENTAL

All samples of nanocomposites NiCo/C were synthesized by the method of IR-pyrolysis of precursors "Me salts – polyacrylonitrile". The precursor was prepared by dissolving a source of metal salts (NiCl2·6H2O, CoCl2·6H2O) and polymer (polyacrylonitrile (PAN)) in dimethylformamide (DMF). The concentration of PAN in DMF solution was 5 wt. %. The concentration of Ni and Co relative to PAN were, respectively, 4 and 16 wt. %. Evaporation of the DMF at temperatures $T \leq 70$ °C to solid residue was carried out after obtain of the homogeneous solution.

The pyrolysis was performed in the IR-camera of the laboratory setup Mila-5000 (Ulvac-RIKO). The process is continuous, but he has several steps: holding at temperature 150-200 °C for 15 min. at each temperature, and the main stage at temperatures of 350, 600 and 800 °C. The heating rate was 25 °/min. The exposure time at the final temperature was 15 min. The process was conducted in vacuum ($P \sim 10^{-2}$-10^{-3} mm Hg.CT.). Pre-aging at temperatures of 150 and 200 °C was performed to remove associated with the polymer solvent and the initial cyclization of PAN.

The structure and phase composition of the nanocomposites were studied by powder x-ray diffractometry. The XRD studies of samples were carried out on a diffractometer Rigaku Ultima IV on monochromatization (monochromator – graphite) CoKα-radiation. The film is focuses on the Bragg-Brentano. Spectra were processed using the software package PDXL, the substructure parameters were determined by approximation, the lattice period was determined by the method of extrapolatio.

Photomicrographs of samples were obtained on a transmission electron microscope LEO912 AB OMEGA, accelerating voltage of 60-120 kV, magnification was of 80×-500000×.

Tne study of the temperature and field dependences of specific magnetization (M) were performed on an automated complex for measurement of physical properties – vibration magnetometer PPMS-14, Quantum Design.

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3. RESULTS AND DISCUSSION

Nanocomposites NiCo / C are synthesized under the action of the IR-heating in the temperature range 350-800 °C. In the work [4] we have shown that in the temperature range 500-800 °C carbonization and the beginning of graphitization of the polymer occurs, accompanied by the release of various gaseous products, among which H2 and CO may be present, which reduce metals. It should be noted that the recovery process occurs in the solid phase of the polymer, so recovery of the metal occurs *in situ*, where atomic hydrogen can participate in the process of recovery, he is formed during the degradation of the main polymer chain in the process of the IR- heating.

Formation of metal nanoparticles is possible in all the presented range of synthesis temperatures according to the results of XRF. The reflexes with angles 2θ = 52°; 60,8°; 91°; 114°, responsible for the phases of metals (Ni, FCC-Co or NiCo alloy), are present on the diffractogram of nanocomposites, synthesized at 350 °C (Fig. 1). The low intensity of these reflexes and a high level of background indicate the small size of the nanoparticles. An estimate of the average size of OCD metallic nanoparticles showed the value of 8-10 nm.

Also amorphous halo is observed in the range of angles 2θ from 20° to 40 °, corresponding to the carbon matrix of nanocomposite.

The growth of the size of the metal nanoparticles occurs with increasing temperature of synthesis. Pronounced reflexes of solid solutions NiCo (2θ = 51°, 60°, 91°, 114°) are seen for samples, synthesized at a temperature of 600 and 800 °C.

The intensity of reflexes of metals with increasing synthesis temperature indicates the increase in the average size of alloy nanoparticles. Average crystallite size of the metallic phase is calculated according to the results of XRF. The calculation showed, that a significant increase in the average size of OCD for the alloy nanoparticles from 35.8 to 80.1 nm (~ 2 times) occurs with increasing temperature of synthesis.

Fig. 2 shows a plot of the diffractogram (50-64°) from the analysis it is obvious that increasing the synthesis temperature from 600 to 800 °C leads to the shift of the maxima of the peaks towards smaller angles, indicating an increase in the concentration of cobalt in the solid solution [7].

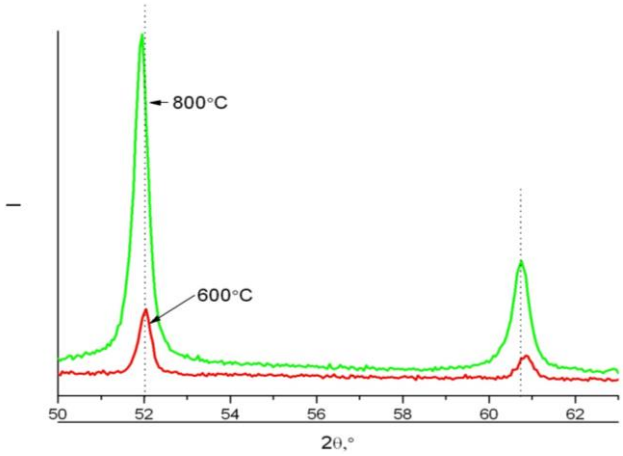

Fig. 2 – A fragment of the diffractograms of nanocomposites NiCo / C, synthesized at temperatures of 600 and 800 °C

Due to the fact that reflexes corresponding to phases Ni, FCC-Co and NiCo are at a very close angle range, phase analysis of the alloy nanoparticles was carried out by the values of the lattice period. It was established, the period lattice for the samples synthesized at 600 °C and 800 °C, was respectively 0.3528 and 0.3541 nm, which indicates an increase of the cobalt content in the alloy. I.e. the formation of intermetallics occurs due to the gradual dissolution of cobalt in the Nickel, the results of studies of the magnetic properties confirmed this.

Fig. 3 shows part of the diffractogram of nanocomposites NiCo / C in the region of small angles (20-40°), characterizing changes in the structure of the carbon matrix of nanocomposite.

The maximum of the halo shifts to larger angles, corresponding to the graphite phase with increasing of synthesis temperature from 350 to 800 °C, and its intensity increases, it shows an increase of the coherent scattering of the crystallites and reduction of amorphous component of the carbon matrix.

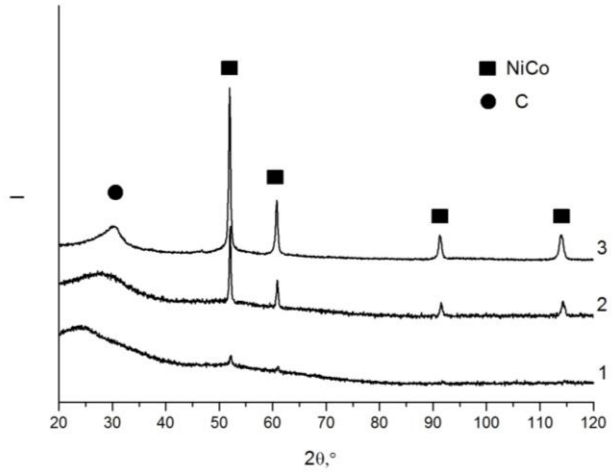

Fig. 1 – Diffractograms of nanocomposites NiCo / C, synthesized at different temperatures: 1 – 350 °C, 2 – 600 °C, 3 – 800 °C

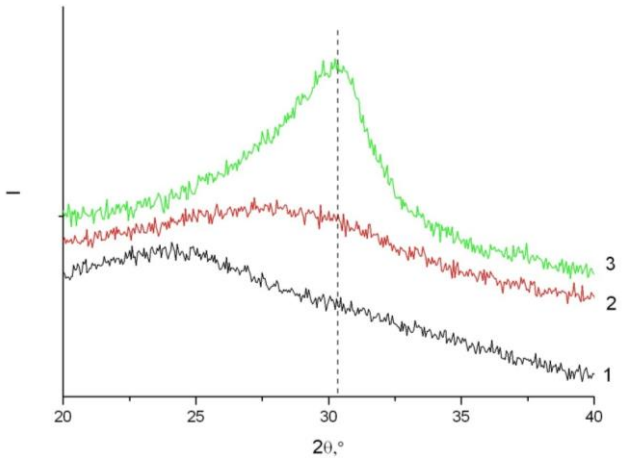

Fig. 3 – Diffractograms of nanocomposites NiCo / C synthesized at different temperatures in the region of small angles: 1 – 350 °C, 2 – 600 °C, 3 – 800 °C

It is found according to the results of PAM, that alloy nanoparticles in carbon matrix nanocomposite are distributed fairly evenly. The dominant size of the nanoparticles increases with increasing the synthesis temperature. With increasing synthesis temperature is observed an increase of the dominant size of metal nanoparticles. Thus, the dominant size of nanoparticles in the temperature range from 350 to 800 °C varies from 10 to 85 nm (Fig. 4).

The study of the magnetic properties of nanocomposites showed, that the saturation magnetization increases with increasing the synthesis temperature (Fig. 5). This dependence is determined mainly by a significant increase in the average size of alloy nanoparticles. For samples, obtained in the temperature range 350-800 °C, the average size of nanoparticles increases from 10 to 80 nm.

The relative content of the superparamagnetic phase partly affects on the magnitude of the magnetization

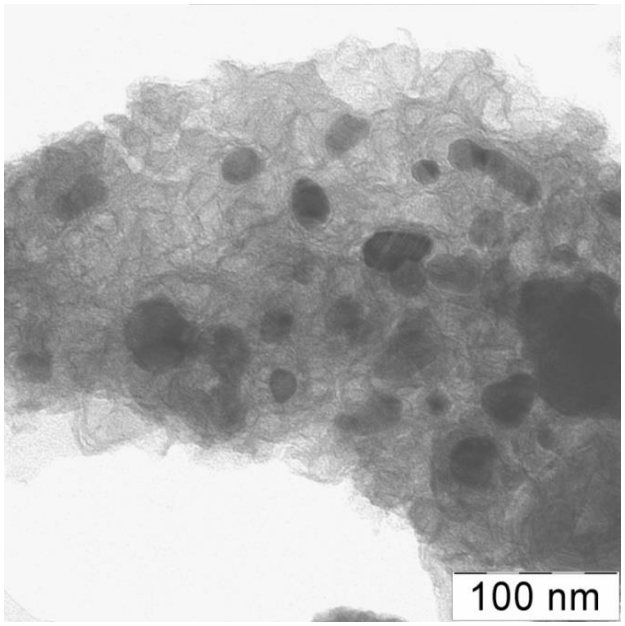

Fig. 4 – Results of PAM for nanocomposites NiCo / C synthesized at 800 °C

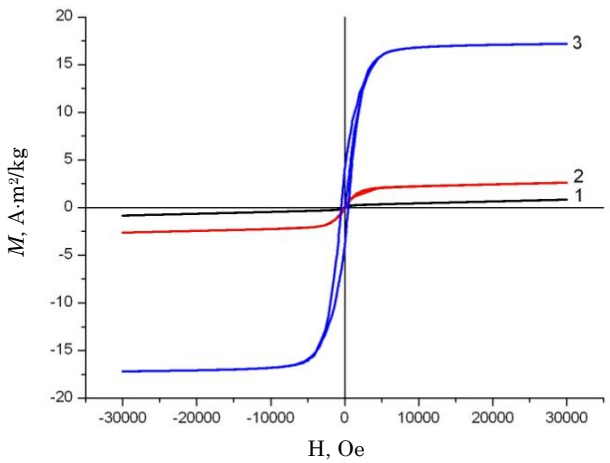

Fig. 5 – Field dependences of the magnetization of nanocomposites NiCo / C, synthesized at different temperatures: 1 – 350 °C, 2 – 600 °C, 3 – 800 °C

of the samples. A significant amount of superparamagnetic nanoparticles presente at the synthesis temperature of 350 °C, as evidenced by the shape of the curve of magnetization. The structuring of the carbon matrix occurs with increasing of synthesis temperature, leading to an increase in the average size of the alloy nanoparticles. The coercive force H_c is increased from 37 to 465 E with increasing temperature from 350 to 800 °C, as well as the residual magnetization Mr from 0.055 to 3.97 A·m²/kg is increased. The growth of the coercive force is defined as the growth in the size of nanoparticles and the increase in the cobalt content in the alloy nanoparticles.

Measurement of temperature dependences of the magnetization of the nanocomposites (Fig. 6) showed, that the specific magnetization increases compared with the original after thermal cycling. This behavior of the magnetization can be determined by the decrease in the content of superparamagnetic nanoparticles small size due to their agglomeration into larger in the recrystallization process of the carbon matrix of nanocomposite. The recrystallization is possible at temperatures, close to the temperature of the synthesis, because the duration of temperature dependences of the magnetization of a lot more than the duration of the synthesis process of nanocomposites, which is manifested in the presence of clear anomalies at 800 °C. The growth of the magnetization, apparently, is determined to improve the structure of the alloy nanoparticles due to the higher grain size and change of the composition of the alloy nanoparticles.

The latter is confirmed by the shift of the Curie point to higher temperatures. It should be noted that several anomalies are observed at the heating protocol – at temperatures of 120 °C, 390 °C, 540 °C and 730 °C.

The anomaly at 120 °C can be explained by the processes of desorption of water vapor, adsorbed by the sample nanocomposite during storage, resulting in a change in mass of the sample and a slight increase of the magnetization. The anomalies at 390, 540, 730 °C can be attributed to the processes of formation of metastable phases of solid solutions of Ni-Co with different composition. This assumption is confirmed by the absence of data anomalies on the cooling curve.

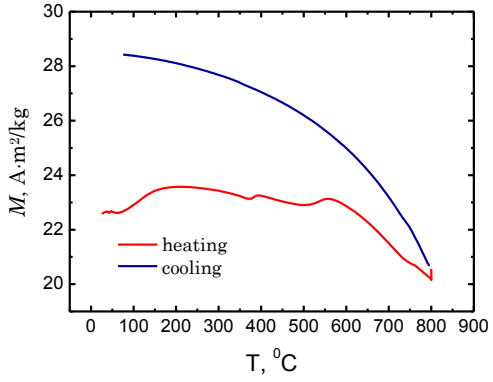

Fig. 6 – Temperature dependence of the magnetization of nanocomposites NiCo / C synthesized at 800 °C

4. CONCLUSIONS

Metal-carbon nanocomposites NiCo / C based on polyacrylonitrile and hexahydratés chlorides of cobalt and nickel are synthesized under the action IR-heating. It is shown that at temperatures of the IR- heating 350-800 °C nanocomposites are formed, in which the nanoparticles of NiCo alloy is uniformly distributed in the graphite-like carbon matrix. It is established, that the composition of the alloy is determined by the temperature of synthesis of nanocomposites. Also with increasing of synthesis temperature the increase in the intensity of the halos is observed, corresponding to graphite-like carbon matrix of nanocomposite, this is associated with the processes of graphitization and indicates the formation of the nanocrystalline structure of the carbon matrix.

The average size of metal particles is determined by the temperature of synthesis and in the range of 350-800 °C is 10-80 nm, respectively. The increase in size is due to the diffusion and agglomeration of the smaller particles. It was established according to the results of PAM that most of the alloy nanoparticles is spherical in shape.

Comparison with results of calculation of the average size of OCD is showed that most of the nanoparticles consists of a single crystallite.

Nanocomposites NiCo/C are ferromagnetics. The magnetization and coercivity depend on the size and composition of the nanoparticles of alloy NiCo. With increasing synthesis temperature from 350 to 800 °C the magnetization increases from 0.055 to 17 A·m^2/kg.

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