JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **6** No 3, 03040(3pp) (2014)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **6** № 3, 03040(3cc) (2014)

The Structure and Magnetic Properties Metal-carbon Nanocomposites NiCo / C on Based of Polyacrylonitrile

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(Received 19 May 2014; revised manuscript received 05 July 2014; published online 15 July 2014)

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. Identification of alloy nanoparticles was carried out by the values of the lattice parameter, which was determined by X-ray analysis and was 0,3533 nm (values of the lattice parameter for Ni 0,3529 nm), this corresponds intermetallics $Ni_{0,5}Co_{0,5}$. By XRD analysis it was determined that an increase in the synthesis temperature of 500 to 800 ºC leads to increase in average size of coherent dissipation of crystallite metal phase.

Keywords: Metalcarbon nanocomposites, Nanoparticles NiCo, Saturation magnetization, Infrared heating.

PACS numbers: 75.50.Bb, 81.05.Zx

INTRODUCTION

Over the past decades, transition metals such as Fe, Co and Ni due to their unique optical [1], magnetic [2], electric [3] and catalytic [4] properties have attracted much attention of scientists and engineers, and also found wide technological application [2, 5, 6]. For example NiCo alloy has high mechanical strength, [7], good wear resistance [8] and anti-corrosion properties [9], conductivity [10], heat resistance [11], the electrical conductivity, the electro catalytic activity [12, 13], as well as interesting magnetic properties [14,15].

Micro-and nano-sized NiCo alloy prepared by various methods: electrochemical reduction [16, 17], mechanical alloying [18], leaching [19] The sol-gel method [20], the thermal decomposition of organometallic precursors, [21], decomposition of polyols [22, 23], decomposition of metal salts by strong reducing agents [24, 25]. Recently, several groups reported about the synthesis of one-dimensional nanoparticle NiCo. For example, in work [26] propose a method for producing an array of nanowires NiCo alloy obtained by joint electrodeposition of Co (II) and Ni (II) into the pores of the alumina, hexagonal NiCo nanowires were synthesized by heterogeneous nucleation in the liquid polyols [22, 23], and had also been prepared by reduction of Co (II) and Ni (II) with hydrazine in the presence of a surfactant [25]. All of the aforementioned synthetic methods require the use of either hard templates or surfactants, or may involve multiple steps. There are also unresolved problems of stabilization of nanoparticles, protection from interaction with oxygen and agglomeration.

The aim of this work was Investigation of the process of obtaining, structural characteristics and magnetic properties of metal carbon nanocomposites obtained by IR-pyrolysis of polyacrylonitrile and compounds of Ni and Co.

EXPERIMENTAL SECTION

Polyacrylonitrile (PAN) was synthesized in the presence of a redox catalytic system according to work [26, 27]. Precursor composition film was obtained from the combined solution in dimethylformamide (DMF) (Fluka, 99.5 %) of polyacrylonitrile dichloride, Dichloride hexahydrate nickel and cobalt (Acros Organics, 99 %) followed by removal of the 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. %, ratio of Ni : Co = 1 : 1.

Pyrolysis was carried out in the IR camera of laboratory setup pyrolysis [26]. Initially, the precursor was heated at a temperature of 150 and 200 °C for 15 min. at each temperature in air. This processing is necessary to remove the solvent. IR-pyrolysis main processing step was conducted in vacuum ($P \sim 10^{-2}$-10^{-3} mm Hg) at temperatures in the range 500-800 °C, for 15 min.

XRD studies of the samples was carried out on a diffractometer Rigaku Ultima IV on monochromated (monochromator - graphite) $Cu_{K\alpha}$-radiation. The scheme shooting is a Bragg-Brentano focusing. Spectra were processed in the software package PDXL, substructure parameters were determined by approximation, the lattice constant was determined by extrapolation.

RESULTS AND DISCUSSION

Metalcarbon nanocomposites were prepared based on polyacrylonitrile (PAN) and compounds of Ni and Co. During the process of IR polymer pyrolysis and forming carbon matrix occur a large amount of gaseous products, including H_2, NH_3, CO which are reducing agents to the metal [27]. Metal recovery process occurs in the solid phase polymer, so that the recovery of the metal takes place *in situ*, where in the recovery process can participate atomic hydrogen can take part and it is formed during the degradation of the polymer backbone during the IR-pyrolysis.

By XRD results it was detected that nanocomposites represent a homogeneous composite, wherein the metal nanoparticles or NiCo alloys dispersed in the carbon

The article was reported at the International Conference «The Advanced Technology, Equipment and Analytical Systems for Materials», Kursk, 13-14 May, 2014

graphite matrix. Fig. 1 shows the diffractograms of nanocomposites obtained in the temperature range of $T = 500$-800 °C.

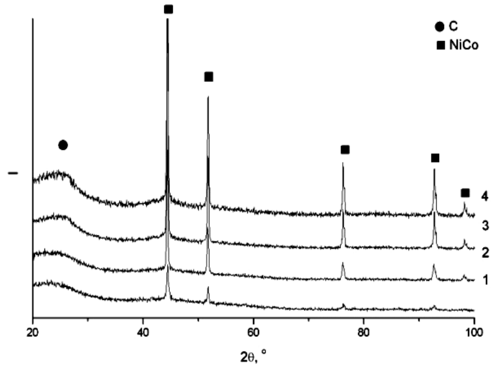

Fig. 1 – Diffractograms of nanocomposite NiCo / C obtained at different temperatures: 1 – 500 °C, 2 – 600 °C, 3 – 700 °C, 4 – 800 °C

In all cases, there are reflexes of intermetallic NiCo ($2\theta = 43{,}5$; $51{,}5$; 76 and 92°). By phase analysis was showed that the obtained nanocomposites contain nanoparticles of NiCo alloy. Because of the lines Co and Ni are in a very close range of angles, identification was carried out by using a value of lattice parameter alloy nanoparticles, which amounted to 0.3533 nm, which corresponds intermetallics $Ni_{0,5}Co_{0,5}$, whereas the Ni lattice parameter is 0.3529 nm.

From the analysis of the diffraction patterns it can be seen the increase in the intensity of all the peaks with increasing temperature synthesis, which indicates an increase in the average crystallite size of the metal phase. The average crystallite size of metallic phase was calculated using the diffraction patterns (Fig. 2).

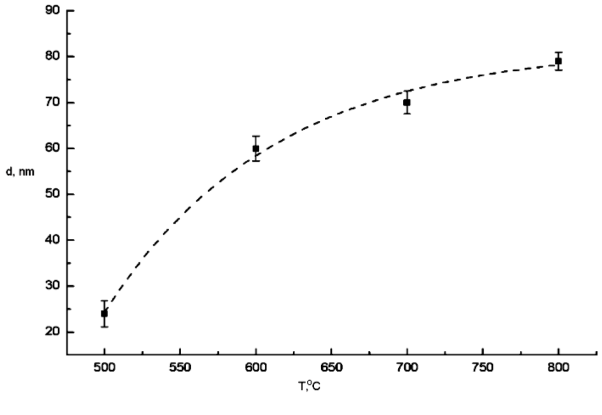

Fig. 2 – Dependence of the average crystallite size (nanoparticles) NiCo from synthesis temperature of nanocomposites

Also it is detected, an increase in the intensity of the halo in the region of angles $2\theta = 20$-30°, which corresponds to the carbon graphite matrix nanocomposites. The asymmetry is defined by nanocrystalline structure of the carbon matrix and the presence of a significant proportion of the amorphous component. With an increase of the synthesis temperature from 500 to 800 ºC maximum of halo is shifted to larger angles corresponding to the graphite phase ($2\theta = 27°$), which indicates an increase of coherent scattering of crystallites and reduction of the amorphous component of the carbon matrix.

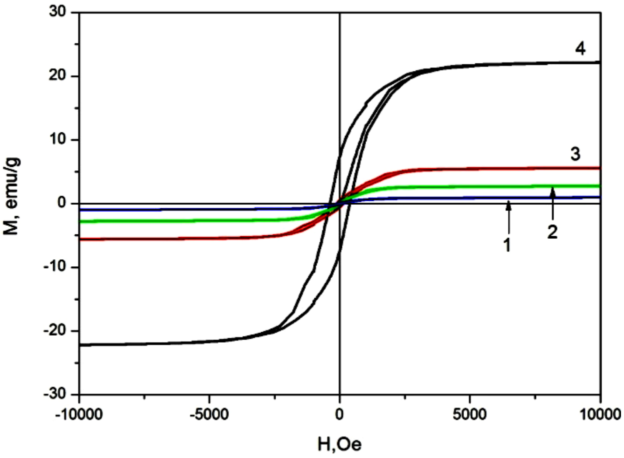

Fig. 3 – Loop of magnetization reversal of the samples of nanocomposites synthesized at different temperatures: 1 – 500 °C, 2 – 600°C, 3 – 700°C, 4 – 800 °C

Study of the magnetic properties (Fig. 3) of the nanocomposite showed that with the increase of the synthesis temperature magnetization the saturation varies from 0,9 to 21,2 emu/g. Samples obtained at temperatures of 500 °C, 600 °C, 700 °C reached magnetization saturation in the fields of 2.2 kOe, 1.4 kOe, and 0.5 kOe, respectively, and for the sample obtained at 800 °C saturation is reached in the fields more than 4 kOe.

The increase of synthesis temperature from 500 to 800 °C leads to a linear increase of the coercive force *Hc* from 54 to 387 Å. Such dependence is determined primarily by a significant increase in the average size of alloy nanoparticles, for samples obtained at temperatures of 500-800 °C the crystallite size was 24-79 nm i.e. at the synthesis temperature of 500 °C there is a significant amount of superparamagnetic nanoparticles with sizes $d \approx 24$ nm. While carbon matrix nanocomposite is characterized by significant fraction of the amorphous component, it complicates indirect exchange interaction and determines the low magnetization of the sample. Growth temperature synthesis leads to the structuring of the carbon matrix and increase the size of nanoparticles alloy.

CONCLUSIONS

Metalcarbon nanocomposites were obtained using PAN and chloride hexahydrate of cobalt and nickel under the influence of infrared heating. The system of PAN / $NiCl_2$ / $CoCl_2$ at temperatures IR pyrolysis 500-800 °C nanocomposite is formed comprising the carbon matrix and NiCo alloy nanoparticles. The average size of the metal particles depends on the temperature obtaining in the range of 500-800 °C and equal to 23-78 nm. The particle size increases with increasing of temperature, and the peak corresponding to the graphite-like carbon phase is growing, it is connected with the process of graphitization. Magnetic properties of nanocomposites depend on the structure and size of the nanoparticles. Magnetization saturation varies from

0,9 to 21,2 emu/g in the temperature range 500-800 °C synthesis, with an increase in Hc values from 53 to 387 Oe.

The work is done with financial support of the Ministry of education and science within the framework of the base part of the state task ‘MISiS’, and also was supported by the grant of the President of the Russian Federation for young scientists and graduate students № СП-4341.2013.1.

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