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Features of Formation of the Nanoparticles of Alloys in Metal-carbon Nanocomposites FeCo / C and NiCo / C on Based Polyacrylonitrile

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By the method of IR-heating the precursor on base of polyacrylonitrile, compounds of iron, cobalt and nickel metal-carbon nanocomposites were obtained, representing an ensemble of nanoparticles of intermetallic FeCo (NiCo), dispersed in nanocrystalline carbon matrix. XRD analysis revealed that the carbon structure of the PAN-based matrix changed from amorphous to nanocrystalline at the processing temperatures in the range 200-700 °C. Thus there is a reduction of metals from compounds released by degradation of the polymer with hydrogen. FeCo alloy nanoparticles formed at synthesis temperatures $T > 500$ °C, in the case of nanocomposites Ni-Co / C alloy nanoparticle formation is possible at $T \geq 270$ °C, which is associated with a lower temperature compared to the recovery of nickel from iron. According to the results of TGA and DSC found that metals are capable of initiating the chemical transformation in the PAN, resulting in reduction start temperature degradation. According to the results of DSC revealed that the formation of nanoparticles is accompanied by release of heat due to exothermic processes occurring in the nanocomposites.

Keywords: Metal-carbon nanocomposites, Nanoparticles FeCo (NiCo), Infrared heating, TGA, DSC.

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1. INTRODUCTION

Nanostructured materials, which are include the nanoparticles or the nanolayers of ferromagnetic metals and alloys in own structure, are causing considerable interest due to the unique optical [1, 2], magnetic [3, 4], electric [5, 6] and catalytic [7] properties, which are manifested in the nanostate, and are find wide technological application [3, 8, 9]. Private interest is the nanoparticles of alloys of the NiCo, FeCo, whose properties are often superior to those of metals and their constituents. Such materials can be used in the systems of magnetic recording [10], the high-frequency devices [11], and the systems of protection from electromagnetic radiation [12] in the range of 4-18 GHz.

Also are observed interesting magnetic properties of nanostructured alloys NiCo [13, 14]. One of the problems in the synthesis of nanoparticles is the need of protection them from oxidation and agglomeration. One solution is the inclusion of nanoparticles in the structure of composites [15-17].

The flow of process of synthesis of nanostructured composite materials containing metal nanoparticles based on polyacrylonitrile (PAN) under the action of IR-heating is largely determined by the physico-chemical properties of the metal compounds used in the synthesis. Also, due to differences in the complex interaction of various metal compounds with polymer, the end result of the pyrolysis process, may lead to significant difference in the structure and properties of the obtained metal-carbon nanocomposites.

In [18-22], it was shown that in the conditions of the IR pyrolysis songs-precursors on the basis of PAN and compounds of various metals such as iron, cobalt, gadolinium, platinum, copper is the formation of metal-carbon nanocomposites. Under the action of intense heat of a non-coherent infrared radiation is carbonation PAN with the formation of graphite-like structure matrix and metal recovery. The result is a nanocomposite, in which metal nanoparticles dispersed in the structure of a carbon matrix. Simultaneous introduction to the composition of precursor salts of two different metals allows obtaining in situ nanoparticles alloys in the structure of nanocomposites [23].

The aim of this work is to study the features of the formation of nanoparticles alloy FeCo, NiCo which are included to the composition metal-carbon nanocomposites based on IR-pyrolyzed polyacrylonitrile.

2. EXPERIMENTAL SECTION

Nanocomposites were synthesized according to [18]. The precursors prepared from the combined solution in DMF (Fluka, 99.5 %) of PAS, iron acetylacetonate hydrate (III) (Acros Organics, 99 %) and cobalt acetate (II) (Acros Organics, 99 %) as well as hydrates of chloride of nickel and cobalt (Acros Organics, 99 %) followed by removal of the solvent at $T \leq 70$ °C. The total concentration of metals in the precursor was 20 wt. %, ratio of metals – 1 : 1.

Synthesis nanocomposites were carried out in the laboratory installation IR-heating MILA-5000 in the temperature range 270-700 °C. Exposure time at the required temperature infrared heating time was 5 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.

TGA and DSC studies were carried out on a thermogravimetric analytical complex Discovery in the temperature range 50-500 °C, the heating rate – 10°/min, the atmosphere – nitrogen, preciseness meas-

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urements of mass – 10^{-5} g. The samples were heated by infrared heater, which allowed compare the results of studies with the results of the thermal transformation of the process of synthesis of nanocomposites.

3. RESULTS AND DISCUSSION

Metal-carbon nanocomposites were synthesized based on polyacrylonitrile (PAN) and compounds Fe (Ni) and Co. By XRD results ascertained that nanocomposites are a composite material in which nanoparticles of metals and alloys were dispersed in the nanostructured carbon matrix. The diffractograms of nanocomposites obtained at $T = 500$, 700 °C (FeCo / C) and $T = 270$, 700°C (NiCo / C) for angles 2θ of 20° to 50° showed on Fig. 1.

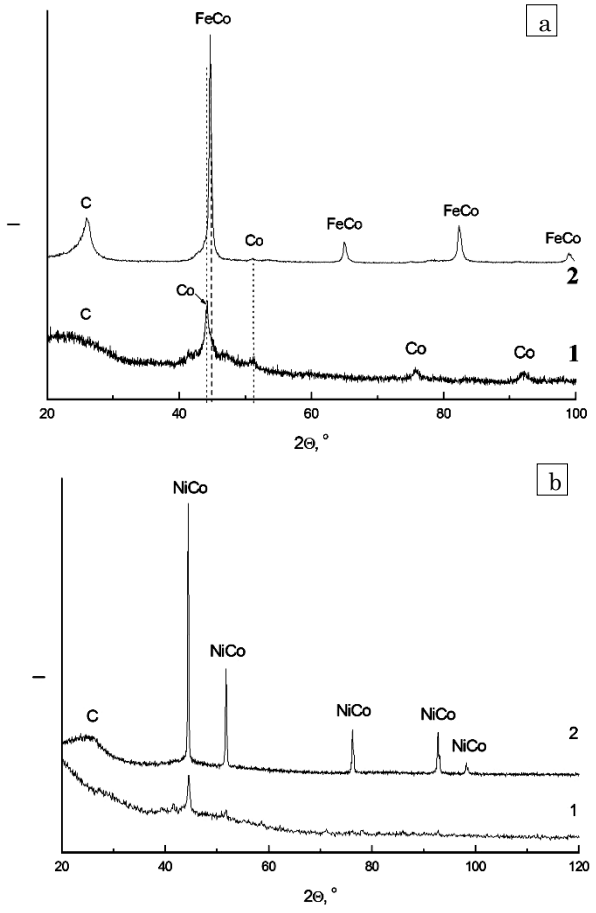

Fig. 1 – Diffractograms of nanocomposite: a - FeCo/C obtained at different temperatures (1 – 500 °C, 2 – 700 °C), b – NiCo/C obtained at different temperatures (1 – 270 °C, 2 – 700 °C)

According to the results of phase analysis was showed that reflections of phase of cobalt and (at the background level) observed in nanocomposites FeCo / C synthesized at the temperature $T = 500$ °C. The reflections of very low intensity can be attributed to very small nanoparticles of carbonized iron. The maximum of peak with a $2\theta = 44°$ has an asymmetric shape (shoulder on the right), which may indicate the beginning of the formation of a solid solution of iron in cobalt. At the synthesis temperature of 700 °C are observed distinct reflexes of alloy FeCo. Composition of intermetallide was determined by the values of the lattice parameter, which equaled to 0.2845 nm.

At the same time, formation of intermetallic phases of nanocomposites NiCo / C is observed even at the synthesis temperature $T = 270$ °C. Also, for all the samples observed increase in the intensity of the peak ($2\theta = 27°$), which corresponds carbon matrix of nanocomposite, that associated with processes of graphitization and the formation of the nanocrystalline structure of graphite (the crystallite size was 2-3 nm at temperature of sinthesis $T = 700$ °C).

Apparently, such differences in structure of nanocomposites based on iron group are caused by physics-chemical properties of metal compounds as well as chemical processes in the temperature range of $T = 100$-400 °C.

So studies were carried out by TGA and DSC to determine the characteristics and conditions of formation of alloy of nanoparticles whith is included in composition of nanocomposites. Found that in the temperature range 50-400 °C stepwise change in sample mass were observed for all samples. The change was 32-34 % weight for samples containing cobalt and iron, and for a sample containing two metals – more than 40 %, which is significantly greater than in PAN – 23 % (Fig. 2).

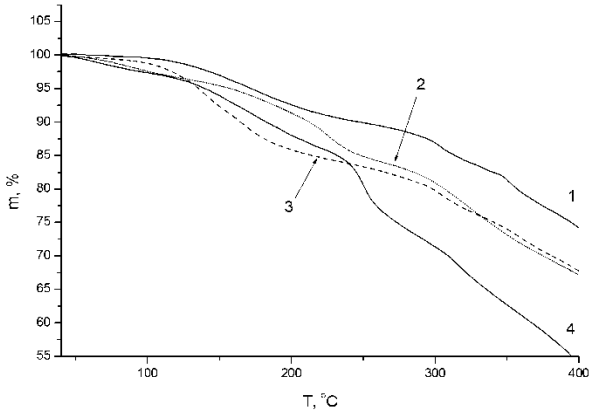

Fig. 2 – TGA of the precursors of nanocompositesFeCo / C: 1 – PAN, 2 – $Co_{ac.}$ / PAN, 3 – $Fe_{acac.}$ / PAN, 4 – $Fe_{acac.}Co_{ac.}$ / PAN

Much stronger mass loss for metal samples are determined primarily by the decomposition of metal compounds introduced into the polymer and accompanied by the release of gaseous products. Also there is a significant shift of the first drop weight range to the low-temperature (over 30 °C). Thus, the presence of the metal leads to a decrease in process temperature, since these compounds react with the nitrile groups of the pan due to the intensive formation of chemical complexes with metals and to facilitates the dehydrogenation process of the polymer chain by separating tertiary atom of hydrogen.

Also there are changes of the mass of samples at range of temperature 150-280 °C, which aren't observed in the PAN, and which are linked, apparently with decomposition metal compounds and metal reduction by hydrogen which is released during the heating of precursors.

Differential TGA curves for these samples are shown in Fig. 3. Several peaks corresponding to the intervals of temperature of changes of mass of the samples is observed in all the dependencies. For mate-

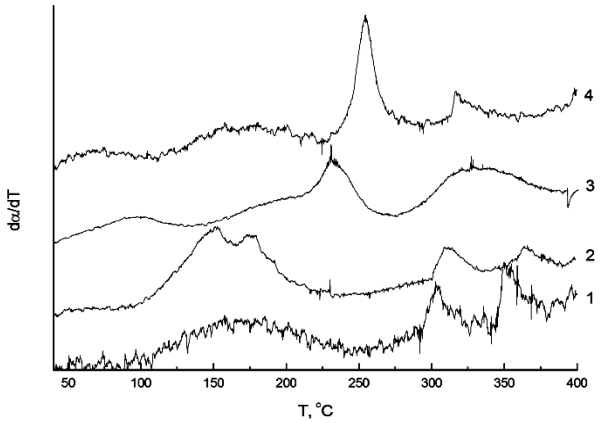

Fig. 3 – Dependence dα/dt of the precursors of nanocomposites FeCo / C: 1 – PAN, 2 – $Co_{ac.}$ / PAN, 3 – $Fe_{acac.}$ / PAN, 4 – $Fe_{acac.}Co_{ac.}$ / PAN

rials comprising metals, observed shift of the first interval of changes of mass to lower temperatures.

For nanocomposite containing simultaneously iron and cobalt, the curve includes peaks that are typical for cobalt-based materials, and materials containing iron. With that the first two peaks are shifted to lower temperatures, i.e. isobserved complex effect of the compounds of metals on the polymer matrix, and the third peak which appropriate for samples containing iron, is shifted to the high temperature region, which indirectly confirms the interaction of iron with cobalt.

Dependence of the mass of the sample heating temperature for nanocomposites NiCo / C has a form similar for precursors which include iron (Fig. 4).

In addition to general trends change of mass during heating, there are differences between the nanocomposites based on iron and nickel. So, change of mass was 27 % for the systems of NiCo-PAN, Co-PAN and more than 35 % for system Ni-PAN in the temperature range 30-350 °C. The most significant changes occur in the temperature range from 50 to 140 °C, which is due apparently by removal of water absorbed nickel chloride from the air; therefore changes of the mass of system Ni-PAN are similar to Ni-Co-PAN at higher temperatures.

From the analysis of the derivative of conversion on temperature (Fig. 5) can be noted that the curve for the system Ni-Co-PAN includes elements of curves for other systems: the peak of 280-330 °C, typical for PAN, shoulder in range 200-270 °C which is typical for system comprising cobalt, peak at 150-220 °C which is typical for system with chloride of nickel.

It should be noted that, as in the case of systems comprising iron, for all samples, including Ni and Co chemical transformation starts at lower temperatures as compared with PAN.

By DSC was revealed that there are some differences in the processes of thermal transformations of precursors of nanocomposites in the temperature range from 150 to 320 °C. Fig. 6 presents a comparison of results for TGA and DSC of nanocomposites FeCo / C and NiCo / C. Endothermic processes are started At temperatures up to 130 °C, which due, apparently, with the removal of the solvent from polymer, and the start of dehydrogenation of the PAN.

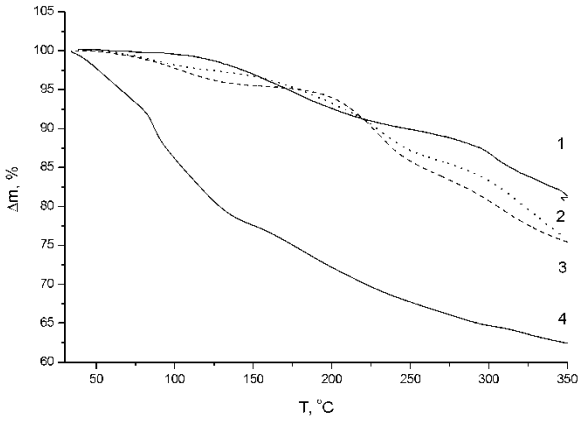

Fig. 4 – TGA of the precursors of nanocomposites NiCo / C: 1 – PAN, 2 – $Co_{chl.}$ / PAN, 3 – $Ni_{chl.}$ / PAN, 4 – $Ni_{chl.}Co_{chl.}$ / PAN

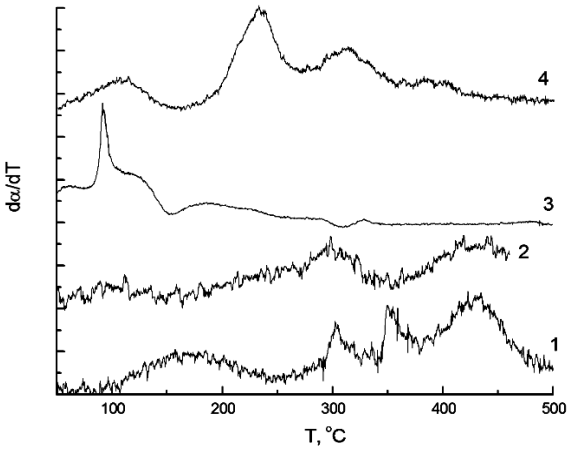

Fig. 5 – Dependence $d\alpha / dt$ of the precursors of nanocomposites NiCo / C on temperature IR-heating: 1 – PAN, 2 – $Co_{chl.}$ / PAN, 3 – $Ni_{chl.}$ / PAN, 4 – $Ni_{chl.}Co_{chl.}$ / PAN

The second interval change mass of precursor is observed at a temperature of 150 °C (NiCo), and 130 °C (FeCo) and is also accompanied by the absorption of heat. This can be attributed to the decomposition processes metal compounds, as well with process of dehydrogenation of the polymer. In the temperature range 230-280 °C for the systems comprising iron and 200-305 °C for the systems based on Ni, there is an abrupt change in mass of the sample, followed by intensive heat generation.

Apparently, at this stage there is a rearrangement of the polymer molecules that accompanied by the formation of intermolecular cross-links, and also by reduction of the metal compounds by hydrogen and by the formation of nanoparticles of metal.

The form DSC curve of nanocomposites NiCo / C differs from that of the DSC curve nanocomposites FeCo / C because at a temperature of 270 °C is formed alloy of NiCo. While in nanocomposites FeCo / C is observed the formation of only cobalt nanoparticles at the temperature range 220-270 °C.

4. CONCLUSIONS

Alloy of nanoparticles FeCo, NiCo in composed of metal-carbon nanocomposites based on polyacrylonitrile under IR-heating were obtained. The formation of

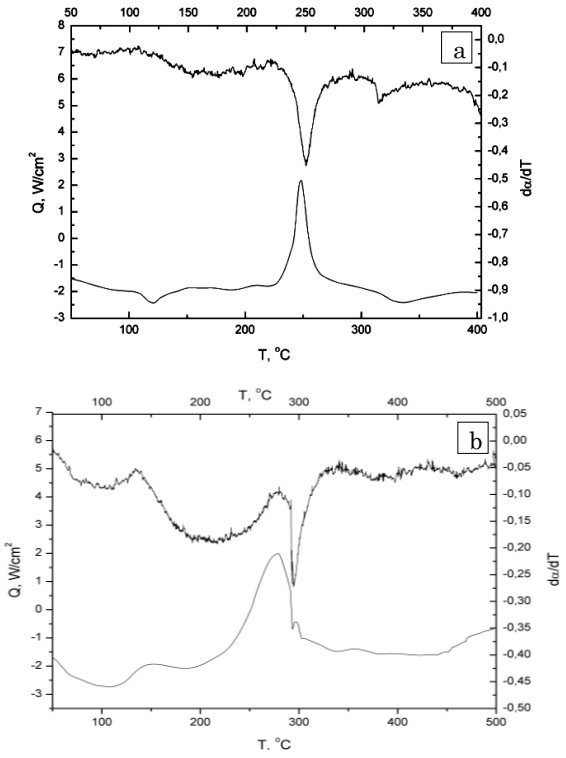

Fig. 6 – The combined results of TGA (top) and DSC (bottom) nanocomposites: a – FeCo / C; b – NiCo / C

the nanoparticles of FeCo alloy occurs at $T > 500$ °C. At lower temperatures of synthesis observed separately the phase of cobalt and probably carbonized iron. It has been shown, that nanoparticles of alloy based on nickel and cobalt as part of the nanocomposites may be formed at low temperatures of syntesis ($T \geq 270$ °C). This is explained by the more intensive evolution of hydrogen due to the degradation of PAN under the influence of nickel, due to comparable temperatures of reduction of these metals by hydrogen and also by forming a solid solution NiCo without changing the type of crystal lattice. According to the results of TGA and DSC found that at the range temperatures 230-280 °C for the systems comprising iron, and 200-305 °C for the systems based on Ni, there is an abrupt change in mass of the sample, which is accompanied by heat, followed by liberation of heat, which is caused by reduction of the metal compounds and the formation of alloy nanoparticles due to processes occurring in the dehydrogenation of PAN.

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