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The Formation and Study of the FeCo Nanoparticles Alloy in Structure of Metal-Carbon Nanocomposites FeCo/C

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The study of the peculiarities of the formation of the nanoparticles FeCo-alloy in the composition of metal-carbon nanocomposites FeCo/C.

Structure, phase composition and kinetic processes of synthesis of nanocomposites FeCo/C by methods of Mossbauer spectroscopy were studied. This allowed us to establish the peculiarities of formation of nanoparticles FeCo alloy in the composition of the nanocomposites. The nanocomposites were synthesized by the IR-pyrolysis at temperatures of precursors of 300 - 800 °C on the basis of polyacrylonitrile (PAN), iron acetylacetonate and cobalt acetate.

Also it is established that an increase in the average size of nanoparticles FeCo with increasing temperature synthesis is occurred. In the temperature range of synthesis of 600-800 °C the size varies from 9-10 to 16-18 nm, respectively.

The features the phase transitions and phase composition of the metal-carbon nanocomposites FeCo / C were studied by Mossbauer spectroscopy. Nanocomposites were synthesized in the temperature range of T = 300-800 °C. It was shown that the samples synthesized at T = 300 °C contains of superparamagnetic nanoparticles of magnetite and amorphous oxide of iron only. The process of forming nanoparticles of alloy FeCo occurs within the temperature range 500-600 ° C due to the recovery of amorphous iron oxide and magnetite as well as them dissolving in a phase of cobalt. The growth of size of nanoparticles of alloy by agglomeration and dissolution of iron in the alloy nanoparticles occurs only at the temperature range of synthesis 600-800 ° C. This is confirmed by a decrease of the content of Fe, which associated with carbon and it is consistent with the results of phase and structural studies, carried out in previous works.

Keywords: Mossbauer spectroscopy, Metal-carbon nanocomposites, FeCo Nanoparticles, XRF-analysis, IR-heating.

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1. INTRODUCTION

Nanostructured materials, incorporating nanoparticles of ferromagnetic metals, are promising for use in various areas of technology: magnetic recording systems [1], high-frequency devices [2, 3], magnetic resonance tomography [4] and biomedicine [5], the systems of protection against EM radiation [6]. Nanoscale FeCo-patterns are allocated among ferromagnetic alloys, because they have one of the highest values of the magnetization. Magnetic properties of these materials strongly depend of the composition and dispersion of the alloy. In some works [6, 7] the effectiveness of using nanoparticles FeCo is shown in the absorbers of electromagnetic waves in the range 4-18 GHz. Currently there are several different approaches to the synthesis of nanoparticles FeCo [6, 9-11, 12-18].

In a number of works [20-22] shown, that in conditions of the IR-pyrolysis of the compositions-precursors on the basis of PAN and various compounds of copper, iron, gadolinium and cobalt the formation of metal-carbon nanocomposites takes place. Under the action of active heating of a non-coherent IR-heating the carbonization of PAN takes place with the formation of graphite-like structure of the matrix and the restoration of the metal. As the result the nanocomposite is formed, in which metal nanoparticles dispersed in the volume of the carbon matrix.

The alternative method, developed by as, allows to synthesize nanoparticles FeCo in the composition of the metal-carbon nanocomposites for one phase under the action of IR-heating, i.e., carbon nanostructured nanocomposite matrix simultaneously is formed in a single process and nanoparticles FeCo- alloy are formed.

In the works [23-25] we showed, that it is possible to synthesize nanoparticles of different alloys in the composition of the metal-carbon nanocomposites, including nanoparticles FeCo.

The mechanisms of formation of alloy nanoparticles not defined in all previous works. The lack of sensitivity of the XRF method was the determining factor. Because, the composition of metal-carbon nanocomposites contains to 20 masses. % metal in the form of nanoparticles, the reflexes of the metallic phases are barely visible because of the strong background. Most strongly it is noticeable for nanocomposites, synthesized at $T \leq 500°$. The use of the method of Mossbauer spectroscopy allows to determine more accurately to the state of iron atoms in the crystal lattice of the metal-containing nanoparticles, which allows reasonable to propose a mechanism for the formation of alloy nanoparticles. It was the aim of this work.

2. EXPERIMENTAL

Polyacrylonitrile (PAN) was synthesized in the presence of oxidation-reduction catalyst system by methodology [20]. The filmes of composite-predecessors were obtained from joint solution in DMFA (Fluka, 99.5 %) PAN, iron acetylacetonate (III) (Acros Organics, 99 %) and cobalt acetate (II) (Acros Organics, 99 %) with the subsequent removal of solvent at $T \leq 70$ °C. The concentration of PAN in the DMFA solution was 5 wt %. Total concentration of metals was 20 wt. %, the ratio of metals was Fe : Co = 1 : 1 to the mass.

Pyrolysis was performed in IR-camera of the laboratory furnace of ИR-pyrolysis in a few steps: aging was at temperatures of 150 and 200 °C for 15 min. respectively, the main stage was at temperatures in the range 300-800 °C. The process was conducted in a vacuum ($P \sim 10^{-2}$-10^{-3} mm Hg.). Treatment at 150 and 200 °C was performed to remove solvent, associated with the polymer and the initial structuring of the PAN. The heating rate was 25 °/min. Exposure time at the final temperature was 5 minutes.

XRF-studies of the samples were conducted on a diffractometer Rigaku Ultima IV on monochromatization (monochromator - graphite) CuKα-radiation. The focusing on the Bragg-Brentano was the scheme of shooting. The spectrums were processed in software package PDXL, options of substructure were determined by the method of approximation, the lattice period was determined by the method of extrapolative.

Messbauer spectra were obtained on the installation Ms 1104 Em in constant acceleration with the source 57Co in the chromium matrix. The powder samples, obtained at synthesis temperatures of 300, 500, 600, 700 and 800 °C, were used. The isomer shift was calculated relative to α-Fe. Mathematical processing of the Mössbauer spectra was performed according to the program "Univem Ms" (Southern Federal University, Rostov-on-Don).

3. RESULTS AND DISCUSSION

It is known [20-21, 25], that in the process of the IR-heating polyacrylonitrile (PAN) undergoes a series of chemical and structural transformations, leading to the formation of a carbon material, having graphite-like structure. When salts of metals introduced into the polymer, such carbon matrix of the nanocomposite is formed, the metal is restored to nonvalence state by hydrogen, released in the decomposition of the polymer, with the formation of nanoparticles.

In the conditions of IR-heating in the temperature range 300-800 °C metal-carbon nanocomposites based on polyacrylonitrile (PAN) iron acetylacetonate and cobalt acetate were synthesized. Metal compounds, used in the present work, at temperatures $T \leq 180$ °C are subjected to decomposition with the formation of oxide forms. The evolution of hydrogen begins at $T = 200$ °C when IR-heating the PAN. The most intensive process of destruction of the polymer, accompanied by the release of various gaseous products, including hydrogen and CO, is observed in the temperature range 300-500 °C. Therefore, the formation of nanoparticles is possible even at temperatures of 250-300 °C. It should

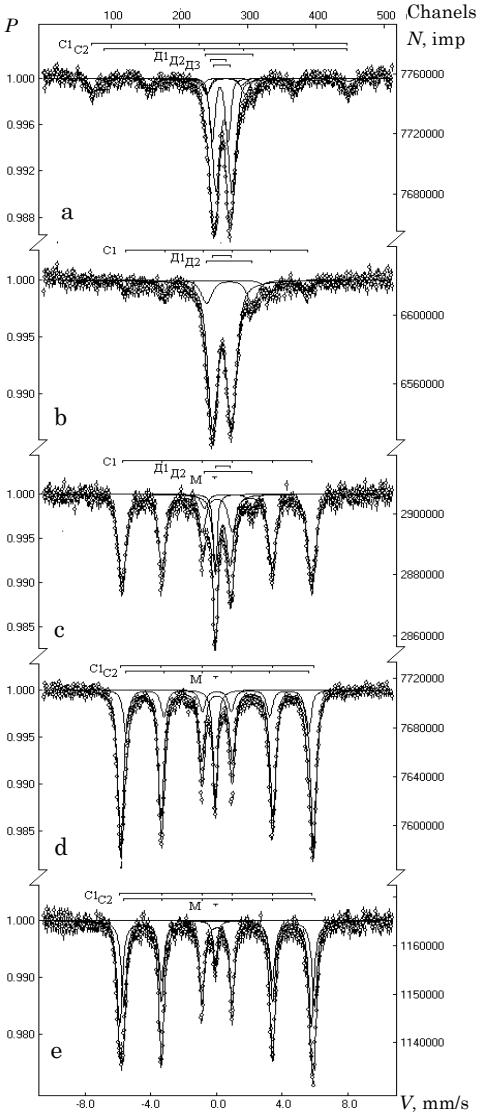

Fig. 1 – Mössbauer spectrum of nanocomposites FeCo/C, synthesized at different temperatures, °C: a – 300; b – 500; c – 600; d – 700; e – 800

be noted, that the recovery process occurs in the solid phase of polymer, so recovery of the metal occurs *in situ*, where atomic hydrogen, resulting during the degradation of the main polymer chain in the process of IR-heating, can participate in the process of recovery.

Studies by Mössbauer spectroscopy allowed setting the features of the process of formation, phase state and structure of iron-containing phases.

Mossbauer spectra of the patternes can be found in on the Figure 1, and their parameters can be found in Table 1 isomeric shift δ, quadrupole splitting Δ, the magnetic field at the nuclei Fe^{57} H, the width of resonance lines G, the square of the components S.

The Mössbauer spectrum of the decomposition products of cobalt acetate and iron acetylacetonate, obtained at 300 °C, is shown in Fig. 1A. It is seen that it consists at 2 and 3 doublets. The sextets belong to the magnetite and due to the Tetra- and octahedral ions iron of the sublattices. The ratio of the squares of sextets from the value 1 : 2 indicates the violation of the stoichiometry Fe_3O_4. The values of quadrupole splitting

and isomer shift of the doublet indicate that they are due to iron ions in octa- and tetrahedral sublattice of superparamagnetic particles Fe_3O_4. The presence of doublet D_1, associated to octahedral ions Fe^{2+} and D_3- with octahedral ions Fe^{3+} points at violation of the electronic exchange between them.

From Fig. 1B shows, that sextets S_1 and S_2, associated with magnetic- ordered particles Fe_3O_4, are absent in the Mössbauer spectrum of products, synthesized at 500 °C. However, sextet S_1 appears in the spectrum, for which the value of the magnetic field at the nuclei Fe^{57} is equal to 344 kOe, which is typical for the alloy Fe-Co (Table 1). This suggests that the formation of nanoparticles FeCo begins at temperatures close to 500 °C.

With further increase of synthesis temperature an increase of the content phase of the alloy FeCo is observed. This is clearly visible in the Mössbauer spectrum of the nanocomposites, synthesized at 600 °C (Fig. 1C). The increase in the content phase of the alloy FeCo is achieved by reducing the content of superparamagnetic particles of magnetite. Moreover, the appearance in the central part of Mössbauer spectrum of the monoline indicates to formation on the surface of the nanoparticles of alloy FeCo of the layer of atoms Fe, coordinated by carbon atoms. Indeed, the existence of such monoline points on a gap exchange links with atoms, localized in the immediate environment of the Fe atoms. The magnitude of the isomer shift of monoline $\delta = -0.1$ mm/s indicates that in the immediate environment of these Fe atoms carbon atoms are.

With increasing the synthesis temperature to 700 °C the integral intensity of the sextets from phase alloy FeCo (Fig. 1D) increases. The presence in the spectrum of the two sextets indicates at the presence in the structure of Fe-Co two inequivalent positions for the atoms Fe, having different number of atoms Co in the immediate environment. The dilution of superparamagnetic particles of Fe_3O_4 is observed simultaneously with formation of the alloy, and the intensity of the monoline increases from the surface iron atoms, having in the immediate environment of the carbon.

The synthesis temperature 800 °C leads to an increase in the intensity of the sextet of the phase of alloy FeCo and a decrease in the intensity of monoline due to the gradual dissolution of iron in the alloy nanoparticles (Fig. 1E). The alloy FeCo also is characterized by two sextets as for samples, synthesized at 700 °C.

Dynamics of phase transformations at synthesis of FeCo is shown in Fig. 2.

The diagrams show, that intensive formation of composites of FeCo/C occurs in the temperature range 500-700 °C and recovery of amorphous iron oxides starts at 500 and ends completely at 600 °C. In the range of synthesis temperatures of 600-800 °C is only an increase of size of nanoparticles of the alloy due to the sintering and dissolution of reduced iron in the alloy nanoparticles. This is confirmed by the decrease of content of Fe, coordinated to carbon.

The study of the structure and phase composition of nanocomposites by the method of XFR showed, that when synthesis temperature is $T = 300$ °C, a quite high is observed on the diffractogram, the reflexes of FCC-Co, BCC-Fe, magnetite (Fe_3O_4) can be distinguished among this background, and also conditionally

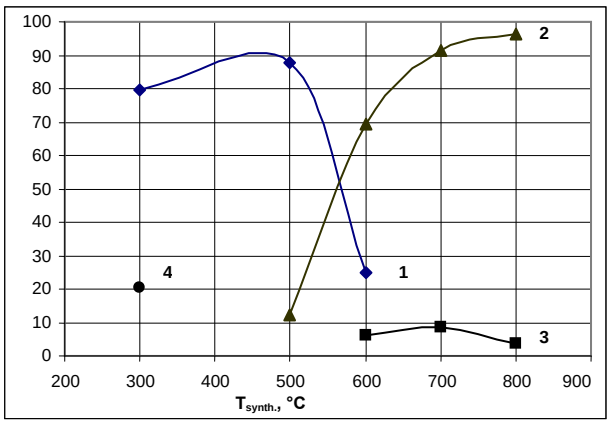

Fig. 2 – The dependence of the distribution of iron on phases from the temperature of synthesis of nanocomposite: 1 – superparamagnetic magnetite; 2 – alloy FeCo; 3 – surface complexes FeC_6; 4 – magnetic- ordered magnetite

Table 1 – The results of Mossbauer studies of the samples FeCo

Sample number	T, °C	Components of the spectrum	δ, mm/s	Δ, mm/s	H, kOe	S, %	G, mm/s	Interpretation
4	300	S1$(Fe^{3+})_{IV}$	0,27	0,01	483	14,9	0,58	Nestekhiometriyaical magnetite
		S2 $(Fe^{2+})_{VI}$	0,62	0,10	459	10,9	0,58	
		D1$(Fe^{2+})_{VI}$	0,86	2.91	0,00	5,5	0,42	
		D2$(Fe^{3+})_{IV}$	0,22	0,97	0,00	19,4	0,40	
		D3$(Fe^{2+})_{VI}$	0,46	0,98	0,00	49,3	0,58	
5	500	S1(Fe)	0,04	– 0,04	344	12,3	0,77	FeCo
		D1$(Fe^{3+})_{VI}$	0,34	1,16	0,00	74,9	0,73	Superparamagnetic magnetite
		D2$(Fe2^{+})_{VI}$	0,79	2,78	0,00	12,7	0,77	
1	600	S1(Fe)	0,03	– 0,01	359	69,2	0,56	FeCo
		D1$(Fe^{3+})_{VI}$	0,40	2,55	0,00	20,4	0,51	Superparamagnetic magnetite
		D2$(Fe^{2+})_{VI}$	0,89	1,11	0,00	4,4	0,51	
		M (Fe)	-0,1	0,00	0,00	6,1	0,28	Surface complexes FeC_6
2	700	S1(Fe)	0,03	– 0,01	366	62,3	0,43	FeCo
		S2 $(Fe^{3+})_{VI}$	0,59	0,02	349	29,0	0,43	
		M(Fe)	-0,08	0,00	0,00	8,7	0,33	Surface complexes FeC_6
3	800	S1$(Fe^{3+})_{IV}$	-0,03	– 0,11	363	58,1	0,33	Fe-Co
		S2 $(Fe^{3+})_{VI}$	0,09	0,13	361	39,2	0,55	
		M(Fe)	-0,08	0,00	0,00	3,7	0,28	Surface complexes FeC_6

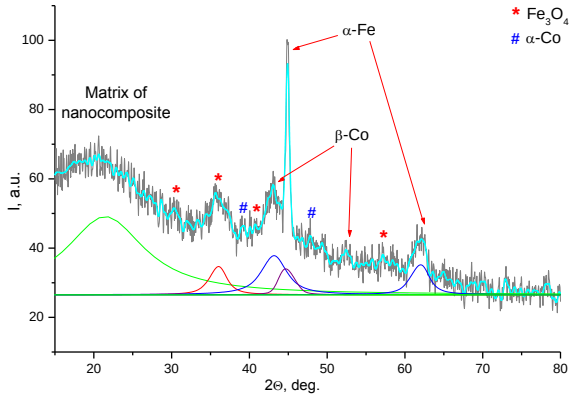

Fig. 3 – The diffractogram of the nanocomposite FeCo/C, synthesized at 300 °C

to mark of the reflexes of HCP-Co or various oxides of iron and cobalt, which have the intensity at the background level (Fig. 1). High dispersion and small size does not allow us to estimate the lattice parameters of these phases.

Amorphous halo, characteristic for the matrix of the nanocomposite at low synthesis temperatures, is fixed in the range of angles $2\theta = 15\text{-}30°$. The matrix is a low-ordered transitional form of material from the polymer to the carbon matrix.

With increasing of the synthesis temperature of nanocomposites up to 500 ° a further carbonation of the matrix of the nanocomposite is accrued, which leads to the formation of low-ordered carbon graphite-like structure. Thus the agglomeration of metal in the nanoparticles accrues at the expense of diffusion processes.

Reflexes of the BCC-iron practically disappear on the diffractogram, which, apparently, is determined by the increase in intensity of the halo of the carbon matrix and the reflexes of cobalt phase (Fig. 4).

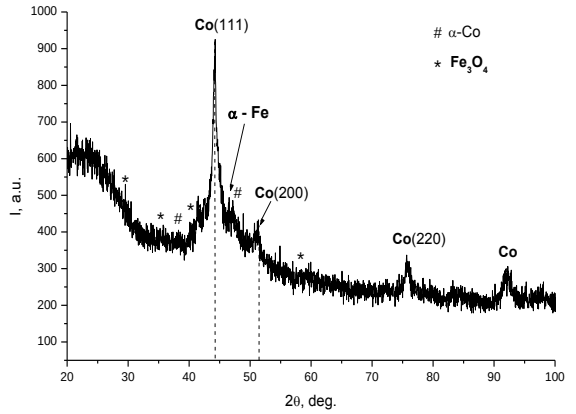

Fig. 4 – The diffractogram of the nanocomposite FeCo/C, synthesized at 500 °C

It is also possible partial dissolution of iron in the cobalt with the formation of solid solution on the basis of the lattice of cobalt, resulting in asymmetry of the reflexes of cobalt. In addition, traces of the phase of HCP-cobalt, magnetite and various oxide forms of iron, the intensity of which is very low, are on the diffractogram.

The calculation of the grating period of the phase FCC-Co showed the value 0,3550 nm, which is characteristic of a solid solution of iron on the basis of cobalt with concentrations, not exceeding 12-16 at. %.

Distinct reflexes of solid solutions FeCo ($2\theta = 45$; 65; 82; 99°), are observed for samples, synthesized at temperatures $T \geq 600$ °C, in this case the nanoparticles, having a BCC- lattice (Fig. 5) are formed.

The increase in the intensity of the halo in the range of angles $2\theta = 20\text{-}30^{o}$ is observed in addition to the reflexes of the metallic phase, which corresponds to the carbon matrix of the nanocomposites. The asymmetry of the halo is determined by the nanocrystalline structure of the carbon matrix and the presence of amorphous carbon. With the increasing synthesis temperature from 500 to 800 ° C the maximum of the halo is shifted in the direction of the angle $2\theta = 27°$ (graphite), the intensity increases. This indicates by the increase in the size of the CSR (coherent scattering region of the crystallites) and the decrease in the amorphous component of the carbon matrix.

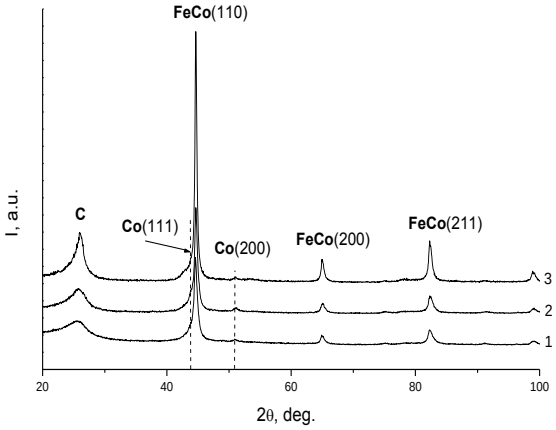

Fig. 5 – The diffractograms of the nanocomposite FeCo/C, synthesized at different temperatures: 1 – 600 °C, 2 – 700 °C, 3 – 800 °C

Thus, the formation of nanoparticles of the alloy occurs in temperature range $T = 500\text{-}600$ °C. It is established, that the period of the lattice of alloy FeCo is 0,2853 nm and weakly depends on the synthesis temperature, indicating the formation of alloy, corresponding to the original ratio of metals $Fe_{0,5}Co_{0,5}$ [27].

The increase in the intensity of reflexes of phase FeCo with increasing synthesis temperature indicates the increase in the average size of the alloy nanoparticles. The calculation showed, that with increasing temperature of synthesis a significant increase in the average size of CSR for the alloy nanoparticles from 8 to 16 nm (~ 2 times) occurs. Apparently, due to diffusion the agglomeration of the smallest metal nanoparticles occurs.

4. CONCLUSIONS

Under the action of the IR-heating metal-carbon nanocomposites FeCo/C on based of polyacrylonitrile, iron acetylacetonate and cobalt acetate are synthesized. Phase transformations in the synthesis process of nanocomposites are studied by the methods XRF and

Mossbauer spectroscopy.

It is established, that at a temperature of 300 °C products of cobalt acetate and acetylacetonate iron are recorded in the spectra, representing the magnetite and X-ray amorphous iron oxides in the form of superparamagnetic magnetite. Investigation by by the methods XRF showed, that in the range of synthesis temperatures of 300-500 °C, the formation of nanoparticles of individual very small size metals at the expense of reduction of iron oxides and cobalt is possible. The increase in the sizes of such particles occurs by diffusion and agglomeration.

The methods XRF and Mössbauer spectroscopy showed, that the process of formation of the nanoparticles begins at temperatures $T \sim 500$ °C due to the recovery of magnetite. The growth of the size of nanoparticles alloy FeCo happens in the temperature range 600-800 °C. So the average size varies from 8-9 to 16-18 nm in the range of synthesis temperatures of 500-800 °C, respectively. In this case, complexes FeC_6 are present on the surface of the nanoparticles, manifested in the Mössbauer spectra in the form of monoline with the isomeric shift – 0.1 mm/s. The concentration of such complexes is significantly reduced due to dissolution of iron in the alloy nanoparticles with increasing synthesis temperature up to 800 °C, which is accompanied by increase in the size of the nanoparticles. It is established according to the results of XRF, that the composition of the alloy nanoparticles corresponds to $Fe_{0,5}Co_{0,5}$, this is in good agreement with the data of Mossbauer spectroscopy.

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