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

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For the first time in the conditions of the IR pyrolysis precursor based on polyacrylonitrile, cobalt acetate and acetylacetonate iron (ratio of metals in precursors Fe : Co = 3 : 1) metal-carbon nanocomposites have been obtained, which are carbon matrix with graphite-like structure, containing buried her nanoparticles of intermetallids of FeCo. It is shown that the phase formation FeCo occurs in the temperature range of obtaining 500-600 degrees centigrade, at $T \leq 500$ degrees centigrade are only two distinct phases metals: HCC-With and BCC Fe. In the structure of nanocomposites obtained at $T \geq 600$ degrees centigrade, at the same time there are nanoparticles of intermetallides and FeCo little content phase fcc-Co or solid solution of cobalt. It is determined that the composition of a metal component nanocomposite satisfies the ratio of Fe, Co, originally specified.

Keywords: Metal-carbon nanocomposites, Nanoparticles FeCo, Raman-spectroscopy, Saturation magnetization, Infrared heating.

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1. INTRODUCTION

Development of methods of nanomaterials with specified properties is one of the priority tasks of modern materials. Scientific and practical interest in metal-carbon nanocomposites is associated with a wide range of areas of potential use, for example in systems of recording and storing information, as electrode materials for fuel cells, as active elements of sensors, biomedical materials, heterogeneous catalysts in chemical processes, and other. Complex physicochemical properties of these materials is determined by the nature of the metal, and electronic structure of carbon phase. The dependence of the phase composition, structure and dimensions of the phases of metal-carbon nanocomposites on the conditions of the process of obtaining opens up the possibility of controlling the properties of such materials.

Substantial interest in nanostructured materials, which contain the composition of ferromagnetic nanoparticles of metals and alloys, caused by specific magnetic properties, manifested nano state: high magnetization and coercitivity, lower Curie temperature, high anisotropy etc. [1-6]. Among ferromagnetic alloys are allocated nanoscale FeCo-patterns because they have one of the highest values of the magnetization, the magnetic properties strongly depend on the composition and dispersion of the alloy. In some works [7, 8] the effectiveness of using nanoparticles FeCo in the absorbers of electromagnetic waves in the range of 4 to 18 GHz has been shown. There are several different approaches to the synthesis of nanoparticles FeCo [6, 9-11, 12-16]. Typical features of the most methods are the methods is a significant number of stages of synthesis, the need for stabilization with the help of surface-active substances, additional reduction step in the atmosphere of hydrogen, a significant duration processes. One of the solutions is to include nanoparticles in in the composition of composites [17-19]. This allows you to control the size of nanoparticles to increase chemical stability, to reduce the density and weight of composite coatings.

The developed technique allows us to synthesize nanoparticles FeCo in structure of metal-carbon nanocomposites for one phase under the action of IR heat, i.e. in the single process of simultaneously formed a nanostructured carbon matrix nanocomposites is the formation of nanoparticles alloy FeCo. In [20-24], 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 [25].

The aim of this work is to receive and study the structural characteristics and magnetic properties of metal-carbon nanocomposites based on the basis of IR pyrolyzed polyacrylonitrile and Fe- and Co compounds.

2. EXPERIMENTAL SECTION

Polyacrylonitrile (PAN) was synthesized in the presence of a redox catalyst system according to [21]. Film precursor composition was obtained 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 %) followed by removal of the solvent under $T \leq 70$ °C. The concentration of PAN in DMF solution was 5 wt. %. The total concentration of metals in the precursor 20 wt. %, the ratio of metal Fe : Co = 3 : 1.

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Pyrolysis was carried out in the IR camera laboratory IR-oven MILA-5000. Precursors was maintained at 150 and 200 °C for 15 min at each temperature. The process was conducted in a vacuum ($P \sim 10^{-2}$-10^{-3} mmHg). This processing is necessary to remove the bound with the polymer solvent and the initial structuring of PAN. This was followed by heating to the desired temperature of the main infrared pyrolysis process, which was 500-800 °C. Exposure time is initiated at the predetermined temperature IR heating was 2 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.

The Raman-spectroscopy was carried out with use of a spectrometer of combinational dispersion of Renishawinvia Raman microscope equipped with Ar$^+$ – the laser which works at length of a wave of 514,5 nanometers. In the range of 100-3000 cm^{-1}, the spectrometer provides resolution of 1,5 cm^{-1}. Maximum power of the laser 5 Wt. For the purpose of receiving a range with the greatest ratio a signal noise the power of laser radiation changes by selection of filters (0,001-100 %). Degradations of samples under the influence of laser radiation it isn't revealed. For receiving ranges of KRS work procedure with a spectrometer of the combinational dispersion, described in a technique "performance of measurements of concentration of the connected hydrogen in carbon films methods of IK-spectrometry and combinational dispersion of light" was used (the certificate on certification of a technique of performance of measurements No. 10/2009, is issued to Rostov Center of Standardization, Metrology and Certification Federal State Institution.

3. RESULTS AND DISCUSSION

Metal-carbon nanocomposites based polyacrylonitrile (PAN) and compounds of Fe and Co were obtained. According to the results of XRD established that nanocomposites are homogeneous material in which nanoparticles of metals or alloys FeCo are distributed in carbon graphite-like matrix. On Fig. 1 presents the pattern of nanocomposites obtained at $T = 600$-900 °C (Fe : Co = 3 : 1).

On the diffraction of all samples in a range of angles 20°-30° is fixed amorphous halo of characteristic weakly ordered carbon structures. Amorphous halo on difractograms is connected with the irregular offset of planes of graphene relative to each other and to the small size of coherent scattering regions of crystalline graphite-like phase [26]. In the process IR-pyrolysis PAN and the formation of a carbon matrix on its basis there is an allocation of a significant number of different gaseous products, including H_2, N_2, NH_3, CO, which are reducing agents for the metal [27]. It should be noted that the recovery is occurring in a solid phase polymer, therefore, the restoration of the material occurs in situ, the atomic hydrogen, which is formed destruction main polymer chain in the process of infrared heating, may by participant the recovery process.

Phase analysis showed that the materials on the basis of acetylacetonate of iron and cobalt acetate contain nanoparticles alloy FeCo, as well as minor maintenance of phase of cobalt.

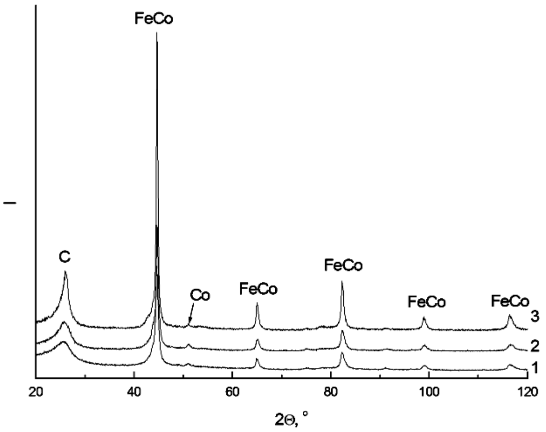

Fig. 1 – Diffractograms of nanocomposite FeCo / C obtained at different temperatures: 1 – 600 °C, 2 – 700 °C, 3 – 800 °C

In all cases, there are distinct reflexes of intermetallic of FeCo ($2\theta = 45$, 65, 82, 99°). In favor of the formation of alloy of FeCo also evidenced by the fact that the reflexes phase fcc cobalt at large angles ($2\theta = 51°$) are virtually absent. Also, are observed an increase in intensity of peak with increasing temperature synthesis, which indicates an increase in the size of nanoparticles. In addition, intensity of the peak ($2\theta = 27°$), corresponding to the carbon matrix nanocomposite, is increased, which is associated with the processes of graphitization and the formation of graphite-like structure with a large crystallite size (from 2 to 5 nmin at temperatures of synthesis nanocomposites 600-800 °C).

Apparently, the process of forming nanoparticles of intermetallic occurs in several stages: first there is recovery of cobalt acetate and the nanoparticles are formed, then iron is reduced and reacted with nanoparticles of Co to form the solid solution. About this evidenced by the fact that the temperature of reduction of compound of the cobalt by hydrogen is significantly lower (~ 200 °C), than the temperature of reduction of compound of the iron (~ 470 °C). The result is a solid solution $Fe_{0,75}Co_{0,25}$ with bcc lattice. Also detected phase which has a cubic face-centered lattice and which refers to fcc - Co or a solid solution of Fe in Co with a concentration of Fe less than 10 %.

According to the results of transmission electron microscopy was determinated that a nanocomposite is a homogeneous material in which the nanoparticles of the alloy FeCo (the dark inclusions) distributed in a nanocrystalline carbon matrix (dark gray). The size of the nanoparticles is determined by the temperature of obtaining of nanocomposites and the dominant size is equal 10-20 nm at the temperature range of 600-800 °C. At the same time the nanoparticles lesser (4-10 nm) and larger (20-35) nm is exist in stock. (Fig. 2).

In order to determine the structure of the carbon matrix more accurately, studies using Raman spectroscopy have been conducted. Each Raman spectra clearly visible bands with maxima in the range of wave numbers 1350-1360 cm^{-1} and in the range of 1560-1580 cm^{-1}.

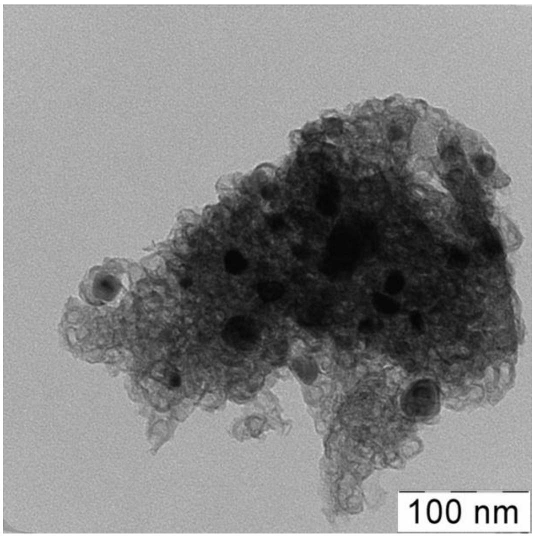

Fig. 2 – The results of the TEM sample nanocomposites FeCo / C, obtained at $T = 800$ °C

The band in the region 1560-1580 cm^{-1} – G-peak which corresponds to the longitudinal vibrations of the C-C bonds in the carbon *sp*2-type hybridization. Disordering the crystal structure of the graphite are broadened peak [28], which is observed for the samples synthesized at $T = 500$°C in comparison with high temperature samples. For structures of graphene and carbon nanotube G - peak position is usually shifted to 1600 cm^{-1}.

In the 1340-1358 cm^{-1} – D- peak is present, which is associated with fluctuations in the deformed C-C bonds with carbon *sp*2-type hybridization, generally corresponds to polycrystalline graphite. With decreasing crystallite size peak position shifts to lower values of wavelengths [29]. What is observed in samples FeCo / C, synthesized in the temperature range $T = 500 \div 900$ °C. Also, the Raman spectra of samples in the band are present in a range of wavenumber 1430-1480 cm^{-1} is responsible for the presence of amorphous carbon. The absence of bands in the spectrum of the sample synthesized at 70 °C, due to the fact that PAN at this temperature no significant chemical reactions leading to occurrence of –C=C– conjugated double bonds.

In [29, 30]it is shown that in the nanocrystalline graphite position of the maximum G-peak corresponds to 1600 cm^{-1}, the intensity ratio $ID/IG = 2$. I.e. due to the small size of the coherent scattering regions of crystallites and lattice distortions, nanocrystalline graphite appears on the Raman spectrum of graphene as a complex of structures.

Presented in Figure 3 the Raman spectra of nanocomposites FeCo / C based on the ratio of D and G-peaks and the shift of the maximum G-band peak to 1600 cm^{-1} in the sample synthesized at 500 °C, suggesting that an increase in the synthesis temperature of the carbon structure varies from matrix to a nanocrystalline structure similar glassy. I.e. graphite-like structure is formed, the size of coherent scattering crystallites increases from 1-2 to 3-4 nm with an increase in the synthesis temperature decreases amorphous component, but significant asymmetry and width of the peak corresponding to graphite, the diffraction pattern can be explained with the irregular displacement of graphene planes each relative to each other.

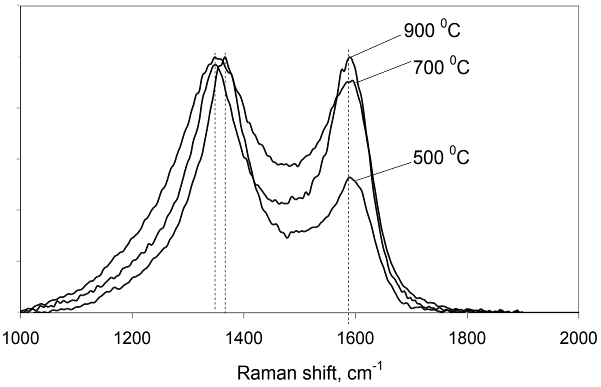

Fig. 3 – Raman-spectra of samples of FeCo / C

Calculations show that with the increase in temperature of nanocomposites synthesis intensity ratio ID / IG tends to unity. According to the literature the ratio $ID / IG = 1$ for glassy and microcrystalline graphite [29]. However glass carbon increased proportion of the amorphous phase, so their Raman spectra have high intensity of Raman scattering in the region 1430-1480 cm^{-1}, which is observed for nanocomposites FeCo / C.

Study of the magnetic properties of metal-carbon nanocomposites FeCo / C showed that the obtained materials are ferromagnetic. The growth of temperature of synthesis leads to growth of the magnetization of the sample (Fig. 4).

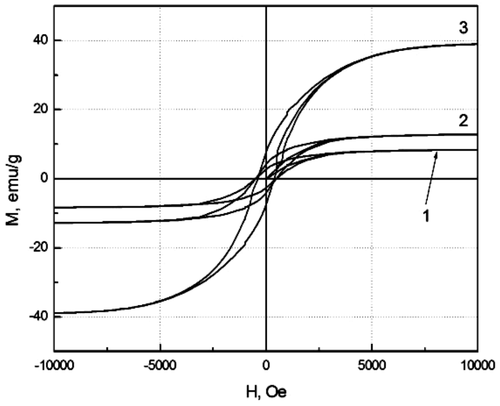

Fig. 4 – Loop of magnetization reversal of the samples of nanocomposites synthesized at different temperatures a – 600 °C, b – 700 °C, c – 800 °C

The saturation magnetization of samples varies from 8 to 39 emu/g with increasing temperature of synthesis from 600 to 800 °C. Thus, the saturation is achieved in fields up to 4 Hoe for the samples synthesized at the temperatures $T \leq 700$ °C. The saturation is achieved in the fields of over 7 Hoe for materials, which were obtained at 800 °C. This dependence is determined primarily by a significant increase in the average size of nanoparticles alloy FeCo, average size was 9-11 nm for materials obtained in 600 and 700 °C, and average size of nanoparticles lies in the range of 18-20 for the samples synthesized at 800 °C. I.e. a significant amount of super-paramagnetic nanoparticles with dimensions $d < 5$-7 nm are formed in the samples formed at the temperature synthesis 600 °C, with a carbon matrix nanocomposite is characterized by a significant share of the amorphous component, which makes it difficult indirect exchange interaction and determines low magnetization of the sample. With increasing temperature synthesis is the structuring of a carbon matrix, leading to the increase of the size of nanoparticles alloy.

Change of coercive force, depending on the synthesis temperature also confirms the presence of small nanoparticles. So for samples synthesized at 600-700 °C, H_c was 500 Oe, and for the sample obtained at 800 °C – 384 Oe, which is consistent with the evolution of the average nanoparticles alloy FeCo. Apparently, for low temperature is achieved the size of nanoparticles which have a maximum coercive force. For example, nanoparticles Co peaked at $d = 8$-12 nm.

4. CONCLUSIONS

Obtained nanoparticles alloy FeCo in structure of metal-carbon nanocomposites based on polyacrylonitrile under the action of IR-heat. It is established that the original ratio of metals entered in precursor affects the phase structure of the nanocomposites. It is shown that with increasing temperature synthesis, the size of nanoparticles alloy FeCo increases with the increasing intensity of peaks corresponding graphite-like carbon matrix nanocomposites that is connected with the process of graphitization. Magnetic properties of nanocomposites are determined by the structure and size of the nanoparticles. The saturation magnetization varies from 8 to 39 emu/g at the interval of temperatures synthesis 600-800 °C with a decrease in the values of H_c from 500 to 384 Oe, associated with the increase in the average size of nanoparticles alloy.

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REFERENCES

1. D. Hisada, Y. Fujiwara, H. Sato, M. Jimbo, T. Kobayashi, K. Hata, *J. Magn. Magn. Mater.* **323**, 3184 (2011).
2. O.V. Fedchenko, A.I. Saltykova, S.I. Protsenko. *J. Nano-Electron. Phys.* **4** No 3, 03016 (2012).
3. A.G. Basov, S.I. Vorobjov, Yu.O. Shkurdoda, L.V. Dekhtyaruk. *J. Nano- Electron. Phys.* **2** No 3, 78 (2010).
4. V.B. Loboda, V.O. Kravchenko, Yu.O. Shkurdoda, *J. Nano-Electron. Phys.* **1** No 3, 58 (2009).
5. T.L. Kline, Y-H. Xu, Y. Jing, J-P. Wang, *J. Magn. Magn. Mater.* **321**, 10, 1525 (2009).
6. Y. Yang, C. Xu, Y. Xia, T. Wang, F. Li, *J. Alloy. Compd.* **493**, 549 (2010).
7. Y. Yang, C.L. Xu, Y.X. Xia, T. Wang, F.S. Li, *J. Alloy. Compd.* **493**, 549 (2010).
8. C. Wang, R.T. Lv, F.Y. Kang, J.L. Gu, X.C. Gui, D.H. Wu, *J. Magn. Magn. Mater.* **321**, 1924 (2009).
9. P. Karipoth, A. Thirumurugan, R.J. Joseyphus, *J. Colloid Interf. Sci.* **404**, 49 (2013).
10. S. Alikhanzadeh-Arani, M. Salavati-Niasari M. Almasi-Kashi, *J. Magn. Magn. Mater.* **324**, 22, 3652 (2009).
11. P.L. Ong, S. Mahmood, T. Zhang, J.J. Lin, R.V. Ramanujan, P. Lee, *Appl. Surf. Sci.* **254**, 7, 1909 (2009).
12. V. Tzitzios, G. Basina, D. Niarchos, Li. Wanfeng, G. Hadjipanayis *J. Appl. Phys.* **109**, 07A313 (2011).
13. K. Za´bransky´, B. Davida, N. Pizu´rova´a, O. Schneeweissa, R. Zborilb, M. Ma˘sla´n, *AIP Conf Proc.* **102**, 1258 (2010).
14. K. Za´bransky´, O. Schneeweiss, *J. Electr. Eng.* **61**, No5, 299 (2010).
15. Z.J. Huba, K.J. Carroll, E.E. Carpenter, *J. Appl. Phys.* **109**, 07B514 (2011).
16. M. Abbas, M. NazrulIslam, B.P. Rao, T. Ogawa, M. Takahashi, C.Gi. Kim, *Mat. Lett.* **91**, 326 (2013).
17. D.J. Kim, M. Pal, W.S. Seo, *Micropor. Mesopor. Mater.* **180**, 32 (2013).
18. M.H. Xu, X.W. Zhong, Z.H. Wang, C. Au, Y.W. Du, *Physica* E **52**, 14 (2013).
19. C. Wang, R. Lv, Z. Huang, F. Kang, J. Gu, *J. Alloy. Compd.* **509**, 494 (2011).
20. L.V. Kozitov, A.V. Kostikova, V.V. Kozlov, M. Bulatov, *J. Nano. Optoelectr.* **7**, 419 (2012).
21. L.M. Zemtsov, G.P. Karpacheva, M.N. Efimov, D.G. Muratov, K.A. Bagdasarova, *Pol. Sci. A* **48** No 6, 633 (2006).
22. G.P. Karpacheva, K.A. Bagdasarova, G.N. Bondarenko, L.M. Zemtsov, D.G. Muratov, N.S. Perov, *Pol. Sci. A* **51** No 11-12, 1297 (2009).
23. E.L. Dzidziguri, D.G. Muratov, E.N. Sidorova, L.M. Zemtsov, G.P. Karpacheva, *Nanotech. Rus.* **5** No 9-10, 665 (2010).
24. M.N. Efimov, E.L. Dzidziguri, E.N. Sidorova, L.M. Zemtsov, G.P. Karpacheva, *Rus. J. Phys. Chem. A* **85**. No4, 660 (2011).
25. D.G. Muratov, L.M. Zemtsov, G.P. Karpacheva, E.L. Dzidziguri, E.N. Sidorova, *Nanotech. Rus.* **7**. No1, 62 (2012).
26. D.G. Muratov, V.V. Kozlov, V.V. Krapukhin, L.V. Kozhitov, L.M. Zemtsov, G.P. Karpacheva, *Izv. VU-Zov: MET.* **3**, 26 (2007) [in Russian].
27. V.V. Kozlov, G.P. Karpacheva, V.S. Petrov, Ye.V. Lazovskaya, *VMS A* **43**, 20 (2001) [in Russian].
28. P.W. May, M.N.R. Ashfold, *J. Appl. Phys.* **101**, 053115 (2007).
29. R. Ramamurti, V. Shanov, R.N. Singh, S. Mamedov, P. Boolchand, *J. Vac. Sci. Technol. A* **24**, 179 (2009).
30. A.C. Ferrari, J. Robertson, *Phys. Rev. B* **61**, 14095 (2000).