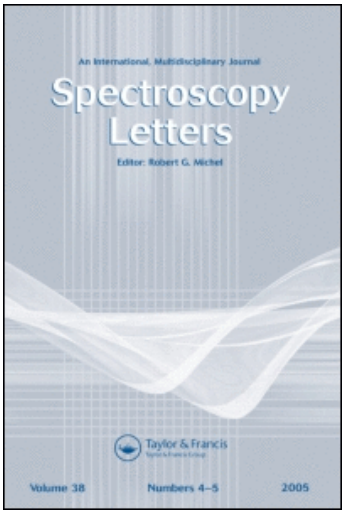

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The Study by Spectroscopy Method of Carbon Nanostructure in Carbonized Ferrochromic Spinel

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ABSTRACT It has been determined that nanostructures of various modifications form during the pyrolysis of hydrocarbons at temperatures of 600° to 850°C in the matrix of iron-chromic spinel. The research performed by means of electron microscopy, X-ray diffraction, infrared spectroscopy, and electron spin resonance (ESR) showed that there were three types of nanosystems in the spinel matrix: crystallites of carbon with sizes of 6–22 nm, multiwalled nanotubes, and carbon filaments.

KEYWORDS nanosystem, multi-walled nanotubes, electron spin resonance, iron-chromic spinel, unpaired electrons

INTRODUCTION

Development and research of carbon nanomaterials have aroused great interest during the past few years. Scientists work actively to obtain fullerenes, carbon nanotubes, nanodiamond, and other types of carbon nanoforms. Nanocrystallic materials are a special state of condensed substance; they are microscopic ensembles of ultrasmall particles with sizes up to several nanometers.[1–4] Usually, carbon nanostructures form as a result of chemical transformations of carbonic materials at high temperatures. Conditions stimulating such transformations are rather diverse. Therefore, the set of methods used to obtain nanostructures varies, too. Carbon filaments and carbon nanotubes can form during the catalytic decomposition of hydrocarbons at rather low temperatures.[4–10] The method of nanotube manufacturing on the basis of carbonization matrices is simple and economic. Therefore, it can be successfully used for nanosystem production with the aim, for example, to study their properties. The appearance of nanophiliform carbon during hydrocarbon decomposition of the metals of the iron subgroup and their alloys is one of the most exotic and practically important processes in view of the mechanism of their formation. By means of different methods of spectroscopy (X-ray, electron microscopy, IR spectroscopy, ESR spectroscopy), this report gives several results of research on the composition, structure, and properties of carbonized iron-chromic spinel

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matrix including the formation in it of several carbon nanostructures. Under certain conditions, iron-chromic spinel under influence of the reactionary environment undergoes some changes.

It should be noted that this material was not used earlier for studying of nanostructure formation during its carbonization in hydrocarbon medium.

The works[5,6] are known in which nanofilaments are formed on iron-aluminum spinel with use of acetylene or methane as a hydrocarbon. In these works, formation of multiwalled nanotubes on iron-chromic spinels is studied under various conditions of their reception. The results of research of these carbon nanosystems have been obtained by various physical methods. It is interesting to study the nanosystem generation on spinels of another type and in natural gas flow.

The choice of iron-chromic spinel as a catalyst for decomposition of hydrocarbons is due to the content of iron in its composition. But it is the presence of ferromagnetic particles of iron, nickel, cobalt, and their alloys in the reactor zone that is a necessary condition of carbonic deposit generation including the nanofilaments with different morphology. Though universally received mechanism of carbonic deposits is unknown so far, one can suppose that most researchers follow the hypothesis[7,8] according to which the carbon nanotubes and carbon nanofilaments form between "basic" particle of catalyst metal and its "microparticle" separated from it as a result, for example, of catalyst erosion. This "microparticle" plays a determinative part in nanofilament formation. The point is that a carbon generated during catalytic decomposition of hydrocarbons diffuses from the frontal side of this "microparticle" to its backside and precipitates as the carbonic deposits.[7,8]

MATERIALS AND METHODS

The iron-chromic spinel carbonization experiments were conducted on a flow-through pyrolysis facility with application of combustible propane–butane mixture. Three sets of samples were carbonized under the following conditions. In the first set of samples, flow rate of mixture was $W = 60$ mL/min and the carbonization time was $\tau = 30$ min. In the second set, the flow rate was $W = 75$ mL/min, and the carbonization time was $\tau = 60$ min. Temperature of carbonization (TC) in the first and the second sets of samples varied in the range of TC = 300°C to 800°C in 50°C increments. In the third set of samples, the rate was $W = 50$ mL/min, the time was $\tau = 180$ min, and the carbonization temperature TC = 600° to 850°C. For all of these sets, the content of carbon in the samples was determined. The amount of carbon deposited on the studied sample surface was determined by the method of combustion of certain quantity of the sample in oxygen followed by absorption of resulting carbon dioxide in a solution of barium hydroxide. Carbon percentage was calculated from the difference between the weights of carbonized samples before and after the combustion. The measurement uncertainty was $\pm 5\%$. After spinel grinding, the fractions with the sizes 10–100 micrometer (mkm) were selected. An elemental composition was determined with the atomic-emission method showing the following sample composition: 8.8% Cr, 21.4% Fe, 10% Al_2O_3, 2% MgO, 12% CaO, and 1% Na. On the basis of X-ray phase analysis data, the sample was identified as chromic iron ore ($FeCr_2O_4$) of spinel group. Fe(II) in it can be substituted by Mg, and Cr by Al or Fe(III). Propane–butane mixture with the composition of C_3H_8 84%, C_4H_{10} 10%, C_2H_6 5%, C_3H_6 1% was the source of carbon. For the experiment, a flowing-type reactor made of heat-resistant chromic steel was used. The reactor was equipped with a heater and rotation gear; determinate temperature in the reactor was held to within 2°C. The reactor was loaded with up to 500 g of the sample. The reaction chamber volume was 3000 cm^3. The carbonization was carried out in the temperature interval 300°C to 850°C with a step of 50°C. The obtained powdered samples were used in further work.

The study of nanostructures in the carbonized spinel matrix was carried out by means of various physical methods: X-ray and phase analysis, electron microscopy, infrared spectroscopy, and ESR. Phase composition of the sample was studied by means of an X-ray diffractometer (DRON-3M). The obtained spectra were identified by means of an X-ray database (Joint Committee Powder Diffraction Data System or JCPDS). The investigations were performed by electron microscope (JEM-100CX) with a resolution of 2 Å. The IR spectra measurements of studied samples was carried out on an IR spectrometer (UR-20) the samples were prepared as pressed pellets of spinel and KBr. ESR spectra were obtained at room temperature on a modernized spectrometer (IRES-1001).

RESULTS AND DISCUSSION

Some peculiarities of carbon deposition formation in the iron-chromic spinel matrix, caused by temperature of carbonization on the samples of the third set, were revealed by means of X-ray and phase analysis. It is determined that the processes of graphite formation and change of size of its crystallites take place in the carbon depositions forming during the pyrolysis of hydrocarbons in the temperature region 700°C to 850°C. The sizes of graphite crystallites were estimated from the analysis of half-width of X-rays peaks. It is determined that the sizes of graphite crystallites increase from $L = 6$ nm at 700°C to $L = 22$ nm at 850°C (Table 1) with interplanar spacing $d = 3.37$ Å[11] as the temperature rises (Fig. 1). This fact also testifies to the compaction of carbon depositions. As the temperature of carbonization rises, nanosizes of crystallites and integrated intensity of graphite crystallites spectra grow because of the increase of resulting carbon amount (Table 1). Minimal width of graphite spectral line at 850°C shows that at this temperature, graphite has more ordered crystal structure than at previous temperatures. The reflexes C(002) on the spectra of measured samples are fixed in the angular range $2\theta = 15.25°$. Moreover, the reflexes of orthorhombic syngony of Fe3C in the angular range $2\theta = 25.75°$C were observed at temperatures of 700°C to 850°C. It confirms the presence of ferric carbide Fe3C in the matrix of carbonized spinel. A precision of the measurements was ±18%. Let us note that the observed graphite crystalline particles were related to that carbon fraction that did not participate in a process of nanosystem formation.

Structure and morphology of the iron-chromic spinel matrix were studied by the method of high-resolution transmission electron microscopy on the third set of the samples carbonized at temperatures of 600°C to 850°C. The electron microscopic images of carbonized iron-chromic spinel at temperature 800°C are shown in Fig. 2. These images show that graphite filaments of both types form in the matrix of spinel.[7–9]

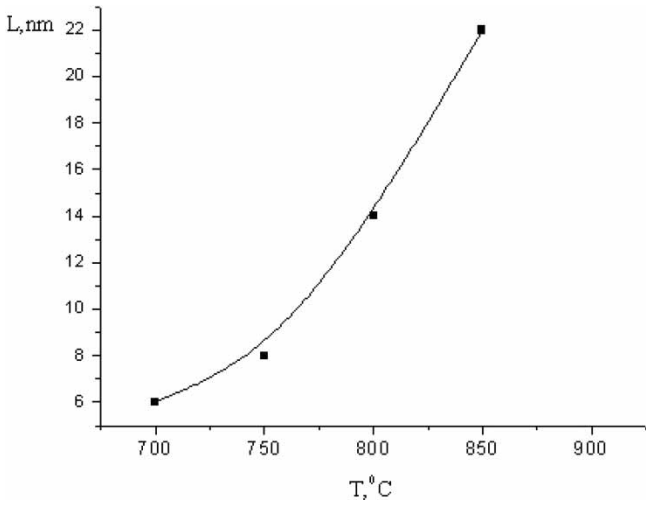

FIGURE 1 Dependence of the Sizes of Graphite Crystallites on Temperature of Carbonization.

The smallest black points that located in the beginning or inside of the nanotubes represent the metal particles. More massive black particles are the metal particles, too. The black formations with more dimensions in Fig. 2a, b, c represent carbonized spinel particles.

Figure 2a shows mainly the filaments with diameter 15–40 nm. Electron microscopic researches show that the nanofilaments of this type most intensively form at temperature 750°C to 850°C. As it can be seen from Figs. 2a,b,c these filaments are multiwalled nanotubes.[7,8,12] Besides these carbon nanotube–type filaments in the carbonized spinel, the filaments of another type—of lamellar

TABLE 1 Temperature Dependence of Percentage of Carbon and Size of Graphite Crystallites under Various Conditions of Carbonization

	C (%)			
T(°C)	$W = 60$ mL/min, $\tau = 30$ min	$W = 75$ mL/min, $\tau = 60$ min	$W = 50$ mL/min, $\tau = 180$ min	L (nm)
Initial	—	—	—	—
500	—	2.01	—	—
550	—	3.5	—	—
600	3.29	3.46	0.38	—
650	3.53	3.61	0.74	—
700	4.89	4.15	1.70	6
750	6.13	6.05	6.56	8
800	7.7	7.89	7.00	14
850	—	—	7.70	22

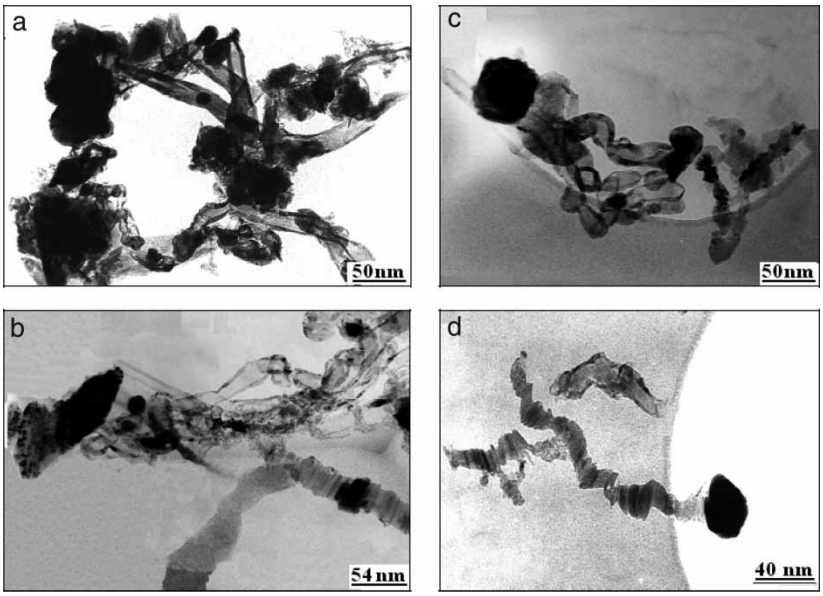

FIGURE 2 Electronmicroscopic Image of Carbonized Spinel at Temperature 800°C: (a–c) Carbon Multiwall Nanotubes; (d) Carbon Filaments of Lamellar Structure.

structure—have been found (Fig. 2d). These filaments are formed by packs that represent a set of graphite planes. There are metal particles with diameters slightly greater than the diameter of filament in the head part of some filaments. The estimations made from Fig. 2d show that the thickness of packs is about 10 nm and the width ranges from 30 to 40 nm.

The investigations by methods of infrared spectroscopy and ESR also indicate the formation of nanosystems in the carbonized matrix of iron-chromic spinel. The infrared spectrum of the third set of iron-chromic spinel matrix carbonized at the temperature TC = 850°C is shown in Fig. 3.

At the temperature 850°C, in the range 502–763 cm^{-1} absorption bands of average intensity are observed and they pertain to the oxides of metals being a part of the spinel composition. As a result of desorption of adsorbed oxygen at the temperature 850°C, in the range 700–1200 cm^{-1} the increasing of the fraction of bonds -O-C-O- and -C-C- occurs. In the spectral range 800–1650 cm^{-1}, there are series of resolved absorption bands of minor and average intensity connected with accumulation of carbonate-carboxylated compounds as well as with the formation of nanosystems. Absorption bands around of 1422 cm^{-1} are caused by the absorption of collective modes of carbon nanosystems[13,14] that can be found in carbon nanostructures. The origin of "collective mode" is due to superposition of the bonds -C-C- and -O-C-O- with vibration, deformation, and electronic nature.

According to their structure, the nanosystems can be considered as three-dimensional analogues of aromatic

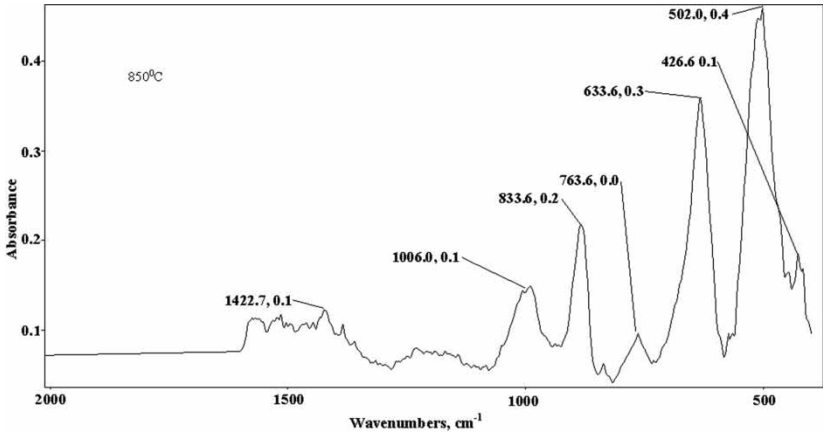

FIGURE 3 Infrared Spectrum of the Spinel Carbonated at 850°C.

compounds.[13,14] Thus, infrared spectroscopic investigations also verify the fact of carbon nanostructures formation in the matrix of iron-chromic spinel.

All three mentioned carbonized sets of samples of iron-chromic spinel were studied by the method of ESR.[15–18] In these systems, the signals of ESR are caused by unpaired electrons of carbon depositions and by ions of ferric iron of spinel matrix. Temperature dependence of ferric iron ions is not reviewed in this paper. Obtained dependencies of concentration of unpaired electrons from temperature of carbonization for the first two sets of samples are shown in Fig. 4. Linewidth of ESR has changed little because of temperature and amounts 0.91–1 mile Telsa (mT) and g-factor $g = 2.013 \pm 0.002$.[19–22] g-factor values for the multiwalled nanotubes in dependence on conditions of their production is estimated from 2012 to 2021. The g-factor quantity obtained by us is in a good agreement with these results. The ESR linewidths are also in a good agreement with the results of other authors for multiwalled nanotubes. The ESR signal of graphite nanocrystallites under conditions of our experiments has not been detected.

As seen in Fig. 4, when the carbonization temperature rises, the concentration of unpaired electrons in both experiments increases and reaches its maximum in the range of temperature 450°C to 500°C. At further temperature increase, the concentration of unpaired electrons starts to decrease sharply. This happens in spite of the increase of carbon content as temperature rises according to Table 1. At the attainment of temperature 650°C, the concentration of free radical states becomes lower than the sensitivity limit of the ESR spectrometer.

However, at the increase of carbonization temperature to 700°C the ESR signals caused by unpaired electrons of carbon appear again. There is no ESR signal from carbon deposition in the first experiment at a further raise of temperature range 750–800°C. On the second set of samples at temperature 750°C the signal also disappeared but it appeared again at carbonization temperature 800°C. On the samples of the third set, the ESR signal is not observed already at temperature 600°C and higher. Our research[15] and also the results of another work[16] show that as content of nanosystems in the volume of the sample increases, the intensity of ESR signal decreases up to complete loss.

It can be supposed that formation of a great quantity of nanosystems takes place also in the studied system, which leads to the ESR signal loss at temperatures 650°C and 750°C in the samples of the first and the second sets. Obviously at these temperatures and hydrocarbon flow rates, there are optimal conditions for the formation of as much an amount of nanosystems as possible.[17] The appearance of the ESR signal at 700°C for the samples of both sets and at 800°C for the second set is rather an unexpected and interesting phenomenon.[14] This question demands additional study. However, it can be assumed that an appearance of the ESR signals at 700°C for the samples of the first and second sets and at 800°C for the third set samples is connected with disturbance of conditions for the formation of as much an amount of nanosystems as possible. It should be noted that in such cases, a sharp decrease of the ESR signal is related to the formation of closed -C-C- bonds by unpaired electrons during the formation of nanosytems. Usually, as temperature of carbonization of the samples rises, the fall in the concentration of the unpaired electrons is explained by formation of graphite plane structures in them. However, we consider that the fall in intensity of the ESR signal at temperature higher than 450°C to 550°C in such systems is caused not only by the formation of graphite plane structures but also by the formation of nanosystems of various morphology. The ESR signal

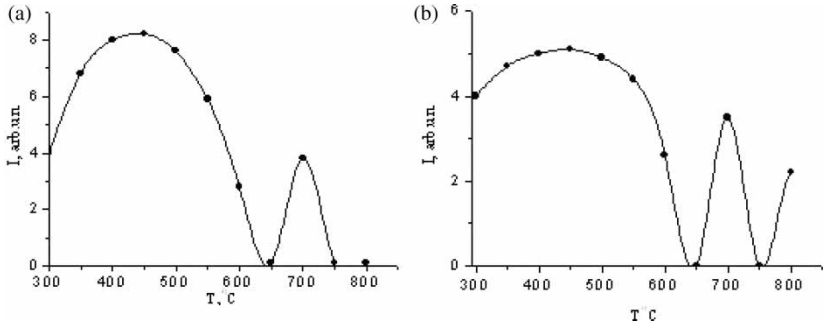

FIGURE 4 Dependence of ESR Signal Intensity on Temperature of Spinel Carbonization: (a) $W = 60$ mL/min, $\tau = 30$ min; (b) $W = 75$ ml/min, $\tau = 60$ min.

loss in the third set of samples at 600°C and higher can be caused by the beginning of formation of different nanosystems. At formation of nanosystems, the most bonds are closed. Perceptible fall in the intensity of the ESR signal during the formation of nanosystems allows using this method for primary selection of optimal conditions of maximum formation of nanosystems at carbonization of some materials. In such systems, formation of numerous -C-C-, -C-O- carbon bonds can cause collective modes of carbon nanotubes.[11]

CONCLUSIONS

The investigation was first carried out with iron-chromic spinel carbonized in natural gas flow. In this spinel matrix, the generation of three types of nanosystems was revealed: nanocrystallites with sizes from 6 nm to 22 nm, multiwalled nanotubes, and lamellar carbon filaments of various morphology. If the generation of multilayer nanotubes and, probably, lamellar filaments in iron-chromic spinel could be (considering a number of publications) somehow forecasted, it is impossible to say anything about forming of graphite nanocrystallites in similar processes on the basis of only one known work.[19] It is early now to say that the nanocrystallite generation is exactly bound up with the iron-chromic spinel peculiarities. Therefore, it is necessary to perform an additional study, but the very fact of such nanocrystallite detecting in the research matrix is interesting. It has been determined by the ESR method that during formation of carbon nanosystems in the matrix of spinel, a sharp decrease of concentration of unpaired electrons takes place because of the formation of closed -C-C- bonds. This fact allows application of the ESR method for initial selection of the optimum conditions for formation of maximum quantity of nanosystems during carbonization of some materials. We suppose that an additional reason leading to increase of the ESR signal reducing rate at the high temperatures of carbonization is the closing of -C-C- bonds during the carbon nanosystem generation.

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