Synthesis and properties of nanostructured materials of the carbon-metal system

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Abstract. As a result of the research, new nanostructured metal-containing materials were synthesized. The phase composition and microstructure of materials have been studied. The regularities of the formation of metal compounds in a carbon matrix have been studied.

Keywords: carbon matrix, phenol-formaldehyde resin, nanocomposite, metal.

Currently, there is growing interest in the creation of nanostructured metal-carbon composite materials. The real interest is associated with the manifestation of surface effects on particles of a nanosized dispersed state.

Obtaining nanostructured metal-carbon composites is a multistage process. The most common methods for obtaining metal nanoparticles on the surface of a carbon matrix are vapor deposition (CVD), pyrolysis, electron beam exposure, carbonization [1–3]. However, the available production methods either require complex hardware and are therefore expensive.

One of the methods for the synthesis of nanostructured carbon materials of the Me - C systems is synthesis in a polymer matrix by pyrolysis [4]. The scheme of the method is shown in Figure 1 [5].

The main polymer matrices for the synthesis of nanocomposites are polyvinyl alcohol, polyacrylonitrile, polyvinyl chloride, etc. [4, 6].

Nanocomposite metal-containing materials are used as electrodes for chemical current sources and water purification devices, high-capacity capacitors, catalysts, gas sensors, drug carriers, MRI, fuel cells, etc. [6 - 8].

The purpose of our work was to synthesize and study the structure of glassy carbon metal-containing composite materials obtained from phenol-formaldehyde resin and carboxylates of transition metals Co, Ni, Cu.

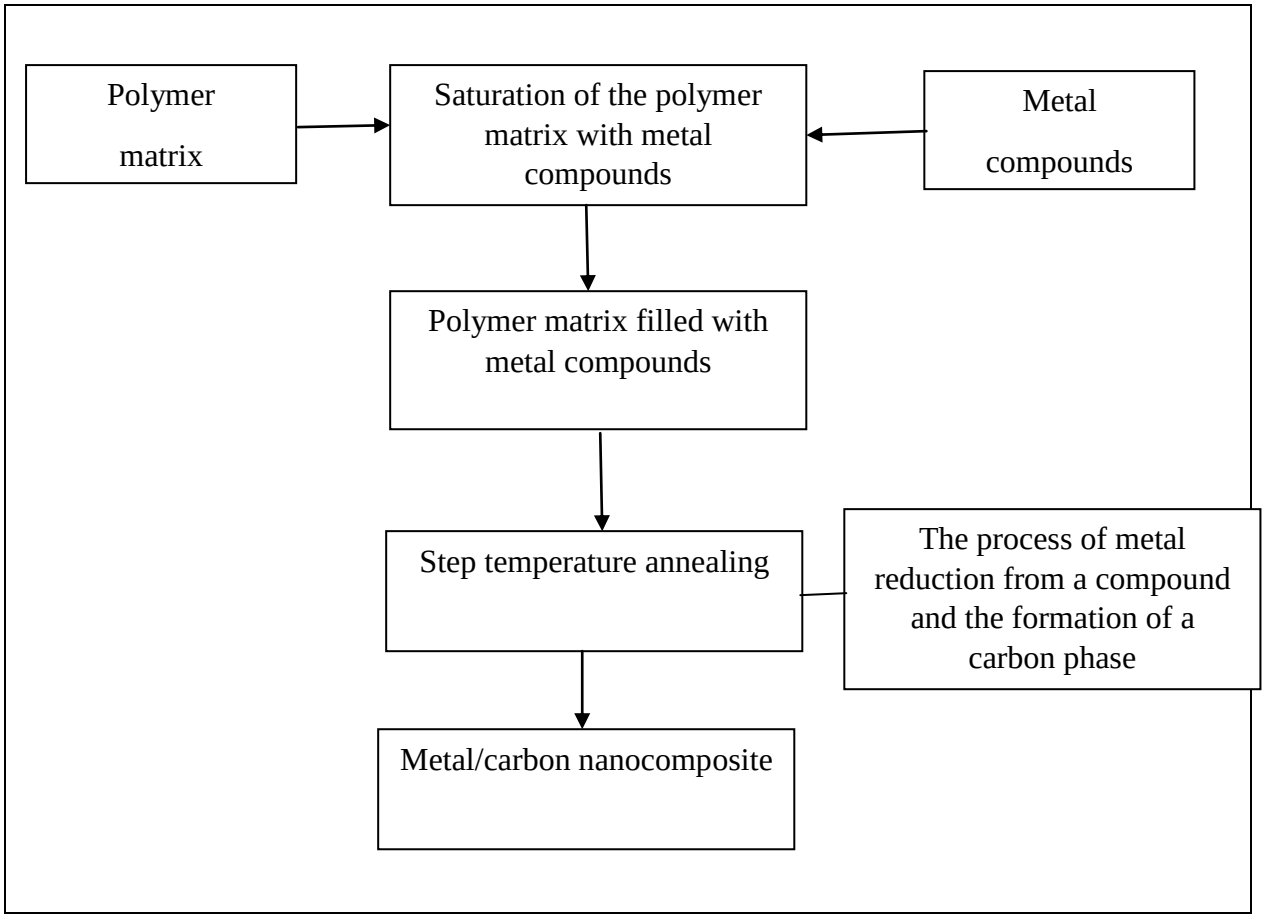


Figure 1. Scheme of obtaining metal-carbon nanocomposites

To obtain a composite material, phenol-formaldehyde resin and 8-hydroxyquinolinates, benzoates, salicylates, phthalates and N-phenylanthranilates of Co, Ni, and Cu were used. The synthesis of metal carboxylates was carried out by ion exchange reactions between sodium salts of organic acids and chlorides of Co, Ni, Cu (scheme 1).

$2R - C(O)ONa + MeCl_2 = (RC(O)O)_2Me + 2NaCl$ (scheme 1)

The binding material for composite materials in our case is phenol-formaldehyde novolac resin, fillers are introduced organic metal salts. Ethyl alcohol was used as a solvent for phenol-formaldehyde resin and metal carboxylates.

The synthesis was carried out according to the method [9]. In our case, the product yield was 70 - 75%. According to the method, water-dioxane solutions of organic acids (8-hydroxyquinoline, benzoic, salicylic, phthalic, and N-phenylanthranilic acids) and a 20% aqueous solution of sodium hydroxide NaOH were used. For the synthesis of Co, Ni, Cu carboxylates, the solutions were heated to 80 - 90°C. When aqueous solutions of sodium carboxylates and transition metal chlorides were mixed, precipitates of transition metal carboxylates precipitated. The resulting substances were purified from impurities of sodium chloride *NaCl*.

The synthesized transition metal carboxylates in a ground powder state were mixed with a ground phenol-formaldehyde resin. to the resulting mixture was poured 95 vol. % ethanol. The resulting mixture was subjected to stepwise thermolysis (figure 2).

As a result of thermolysis, an opaque, glassy porous black shiny material was obtained.

Scanning electron microscopy, X-ray phase analysis, and X-ray microanalysis were used to study the synthesized composite materials. The structure and chemical composition were determined by electron microscopy using a Jeol JSM-7001F electron microscope. The phase composition of the composites was determined using a Rigaku Ultima IV X-ray powder diffractometer.

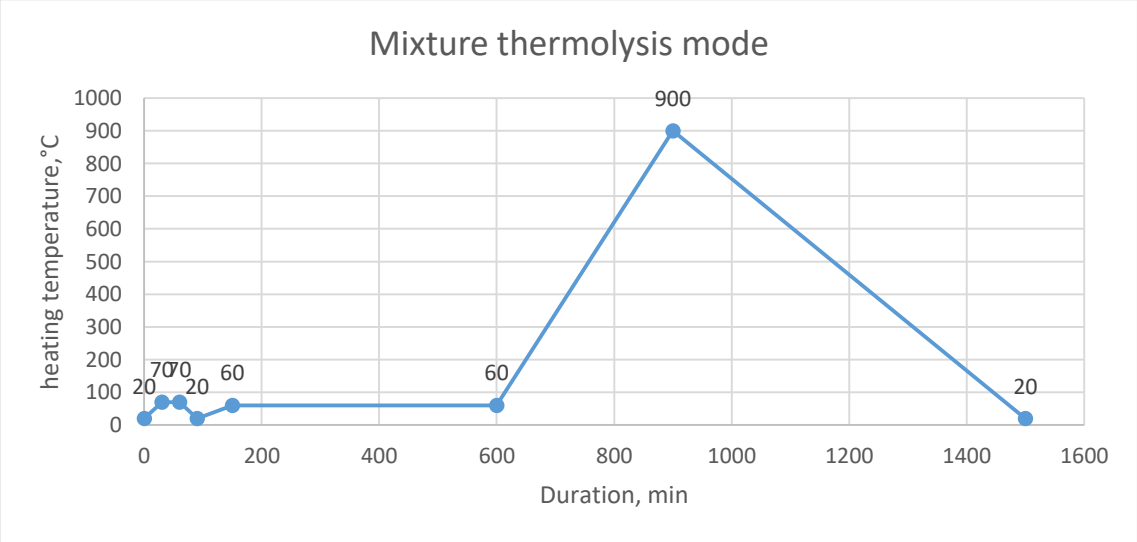


Figure 2. Graph of the heat treatment mode of the mixture

X-ray phase analysis of organic salts made it possible to confirm the formation of only a few compounds: $Cu(HPhtal)_2 \bullet 2H_2O$, $Co(HSal)_2 \cdot 4H_2O$, $Ni(HSal)_2 \cdot 4H_2O$, $Cu(HSal)_2 \cdot 4H_2O$. The rest of the connections do not yet have a resolved structure. The assumption about the existence of new synthesized carboxylates was based on a comparison of X-ray diffraction patterns of the synthesized product and reagents.

When studying the composites, the morphological characteristics of the samples, their local and average chemical composition, and the uniformity of metal distribution in the glassy carbon matrix were evaluated. In this case, two samples were taken from the sample - from its upper and lower parts. This made it possible to estimate the solubility of transition metal compounds in the total solution by the ratio of the average metal content in the upper and lower parts of the sample, since incompletely dissolved particles of these compounds settled in the lower part. It can be assumed that in samples containing similar amounts of metal in the upper and lower parts of the sample, the solubility of the salt is higher.

The homogeneity of the composite can be estimated as the ratio of the measured metal concentrations indicated in the table as a fraction, in which the numerator indicates the concentration at the top and the denominator at the bottom of the composite (table 1).

Table 1 – Metal concentration in the composite, wt. %. The numerator indicates the concentration in the upper part, and the denominator - in the lower part of the composite

Cation	Anion				
	8-hydroxy-quinolinate	Benzoate		Salicylate	Phthalate	N-phenyl anthranilate
Co	5.20/15.44	0.67/-		2.46/-	5.10/22.94	3.31/3.61
Ni	4.50/4.72	-/11.43		2.19/-	4.02/7.56	3.78/16.52
Cu	2.66/4.10	[a]1.24/-	[b]0.76/-	2.13/-	3.94/5.73	1.17/4.08

a – DMF washed, b – recrystallized from DMF.

Analysis of these data indicates that nickel (II) 8-hydroxyquinolinate, copper (II) phthalate, and cobalt (II) N-phenylananthanilate had the best dissolution in phenol-formaldehyde resin, and during heat treatment they retained high dispersion. This indicates that, firstly, the listed anions formed a strong bond with the phenolic rings, and, secondly, the listed cations exhibit a high coordination number. As a result, they coordinated the electrons of the phenolic rings on themselves. It follows from this that the formed coordination structure remained strong during thermolysis. This ensured that during the heating process, metal particles retained their position in the resin structure, and then in glassy carbon.

The sizes of metal particles observed using electron microscopy are summarized in table 2. In more than half of the cases, the sizes differ by one or two orders of magnitude, and in many of these cases a bimodal distribution can be noted. In some cases, the irregular particle shape may suggest that the large particles are agglomerates of smaller crystallites. To estimate the average crystallite size, the sizes of the coherent scattering regions were determined, calculated from the

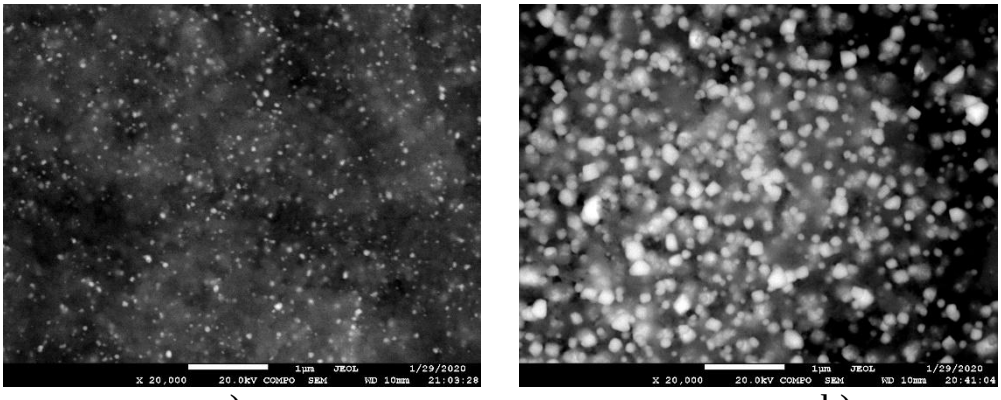
half-width of the X-ray reflections (table 3). Among other salts, salicylates are smaller and have a narrower particle size distribution.

Figure 3 shows the typical morphology of a cobalt nanocomposite in a glassy carbon matrix prepared using cobalt phthalate. The images obtained in the reflected electron mode show a dark glassy carbon matrix and light inclusions of a heavier element (cobalt). Obviously, in the lower part of the material, the concentration of metal inclusions is higher, which indicates that cobalt phthalate particles settle in the alcoholic solution of the resin. Cobalt particles are finer in the upper part of the sample (20 - 100 nm) compared to the lower part of the sample (100 - 250 nm).

Table 2 – The size of metal particles in the composite according to microscopy data, microns. The numerator shows the size at the top, and the denominator - at the bottom of the composite

Cation	Anion				
	8-hydroxy-quinolinate	Benzoate		Salicylate	Phthalate	N-phenyl anthranilate
Co	0.01 – 0.7/ 0.02 – 0.7	0.01 – 0.2/-		0.02 –0.03 /-	0.02 –0.07/ 0.07 – 0.2	0.02 – 0.5/ 0.03 – 1.0
Ni	0.02 – 0.4/ 0.01 – 0.3	-/0.01 – 0.3		0.01 – 0.1/-	0.03 – 3.0/ 0.01 – 0.3	0.05 – 0.5/ 0.05–1.0
Cu	0.1 – 2.0/ 0.04 – 1.0	[a]0.07- 1.0/-	[b]0.7- 1.0/-	0.7 – 1.0/-	0.02 –0.40/ 0.02 – 3.0	0.05 – 5.0/ 0.03 – 4.0

a – DMF washed, b – recrystallized from DMF.



a) b)

Figure 3. Morphology of Co/glassy carbon nanocomposite obtained using cobalt phthalate: a) in the upper part, b) in the lower part of the sample

Table 3 – Size of areas of coherent scattering of metal particles in the composite according to X-ray phase analysis, μm.

Cation	Anion				
	8-hydroxy-quinolinate	Benzoate	Salicylate	Phthalate	N-phenyl anthranilate
Co	0.079	0.094	0.004	0.070	0.085
Ni	0.038	0.028	0.026	-	0.072
Cu	0.046	0.5/0.050*	0.050	0.063	0.080

*in the numerator – DMF washed, in the denominator – recrystallized from DMF

According to these data, it can be concluded that the particles are in a nanostructured state. Moreover, the smallest size is possessed by nickel and cobalt nanoparticles in the case of 8-hydroxyquinolinate, benzoate and salicylate anions for nickel and salicylate for cobalt. This indicates a high solubility in phenol-formaldehyde resin.

X-ray phase analysis was used to obtain data on the phase composition of the obtained composites (table 4).

Table 4 – The content of metal (in the numerator) and graphite (in the denominator) in the composite according to X-ray phase analysis, wt. %.

Cation	Anion				
	8-hydroxy-quinolinate	Benzoate	Salicylate	Phthalate	N-phenyl anthranilate
Co	28/72	17^{a}/27	47^{e}/20	40/60	40/60
Ni	100/0	100/0	95^{h}/2	0^{d}/0	40/60
Cu	97^{c}/0	27^{b}/0 (10^{g}/0) *	45^{f}/0	97/3	100/0

Notes to Table 4: *without brackets – salt washed with DMF, in brackets – salt recrystallized from DMF. Together with the metal phases, the composite material also contains oxide phases: a – 29 % CoO, 28 % Co_3O_4, b – 73 % Cu_2O, c – 3 % Cu_2O, d – 20% Ni_3S_2, 80% Ni_9S_8, e – 10 % Co_3O_4, 23 % CoO, f – 55% Cu_2O, j – 70 % Cu_2O, 20 % CuO, h – 3% NiO.

As a result of the data obtained, it can be concluded that the phase composition of the obtained materials is different. In addition to the phases of the reduced metal and graphite, metal oxides are formed from the thermolysis of the anion. This is due to the strength of the bond between the metal cation and the acidic anion. As a rule, the resulting multicomponent residue consists of a mixture of nearby oxides or a mixture of elemental metal and its lower oxide.

As a result of the research carried out, the following conclusion can be drawn. First, a new technique was developed for the synthesis of new carbon nanocomposite metal-containing materials. These materials have been received. Secondly, the composition and structure of the

obtained materials were studied. Based on these results, assumptions were made to explain the homogeneity and heterogeneity of the material in terms of volume and the composition of the phases that form the material.

From the study of the obtained composite materials, it can be concluded that the most uniform distribution of metal particles over the volume of the composite material was observed in the case of using Ni (II) 8-hydroxyquinolinate, Cu (II) phthalate, and Co (II) N-phenylanthranilate. During the thermal decomposition of metal salts in the phenol-formaldehyde matrix, mainly metal particles were formed in the case of the use of Co (II) and Cu (II) 8-hydroxyquinolinates, Ni (II) benzoate, Co (II) and Cu (II) phthalates, and Co (II), Ni (II) and Cu (II). In this case, the largest particle size of the reduced metal (more than 2 μm) was observed in the case of using Cu (II) N-phenylanthranilate and Ni (II) phthalate, and the smallest particle size (about 10 nm) - in the case of using Co 8-hydroxyquinolinates and benzoates, Ni, salicylate and Ni phthalate. Analysis of the results showed that salicylates Co, Ni, Cu give composites with the most monodisperse and fine metal particles. Phthalates follow, the rest of the salts close the row.

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