

The Synthesis of Metalcarbon Nanocomposite Ni / C on the Basis of Polyacrylonitrile

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Metalcarbon nanocomposites based on polyacrylonitrile and nickel chloride are synthesized under the influence of infrared heat. The resulting materials represent a system of carbon matrix formed during the carbonization of PAN, and distributed in it nickel nanoparticles. The average size of the nanoparticles in the nanocomposite was 15-25 nm. It was found that the distribution of nickel nanoparticles sizes is determined by temperature synthesis nanocomposite. Thus with increasing temperature, the predominant average particle size of the metal increases, and the distribution is spread and shifted toward larger sizes.

Keywords: Metalcarbon nanocomposite, Carbon matrix, Nanoparticles of nickel.

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1. INTRODUCTION

Currently functional nanomaterials are of great interest to researchers because of its unique properties, which manifest themselves in the nanostate. In the nanostate for the materials new opportunities are opened up in both the theoretical aspect and the experimental use. Special interest is composite nanomaterials. The composite materials comprising nanoparticles 3d-metal (Fe, Co, Ni), and their oxides are of interest from the viewpoint of use as heterogeneous catalysts for petrochemical processes [1, 2], the growth of carbon nanotubes [3, 4], components of dispersed radar absorbing media [5, 6, 7].

Currently, there are several groups of methods and approaches to the formation of nanomaterials including nano-sized metal particles. Regardless of the approach, the controlled synthesis of nanoparticles with a narrow size distribution and well-defined structure is one of the main problems.

The aim of this work is to obtain the metalcarbon nanocomposites based in polyacrylonitrile under IR-heating including nickel nanoparticles dispersed in the carbon matrix, and the study of the structural characteristics of the synthesized material.

2. EXPERIMENTAL

Metalcarbon nanocomposite are obtained by IR annealing of polyacrylonitrile (PAN) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. Precursors nanocomposites were prepared by co-dissolving PAN and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in dimethylformamide (DMF, Fluka, 99.5 %) followed by removal of solvent. The concentration of PAN in DMF solution was 5 wt %. And nickel – 30 % by mass. Re calculation for chloride hexahydrate.

Pyrolysis was carried out in the IR-camera of pulse photon annealing installation. IR-annealing was done in a two steps operation: preliminary annealing in air at 150 °C and 200 °C for 15 min, during which the solvent is removed and PAN original structuring performed, and basic annealing in an inert atmosphere at

a desired intensity of infrared radiation that heats the sample to a temperature in the range 400-700 °C. The holding time at the final temperature was 120 s. The heating temperature of the sample was fixed with the chromel-alumel thermocouple.

Calorimetric study carried out on a differential scanning calorimeter (DSC) Q20 (TA Instruments, USA) at a heating rate 10 °C/min in a range of 50-350 °C. Measurements were performed in a nitrogen flow of 50 ml/min. Pattern in the form of powder was placed in a platinum crucible is sealed.

Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer Discovery TG TM (TA Instruments, USA) in the temperature range 50-700 °C at a heating rate of 10 °C/min under nitrogen flow rate of 50 ml/min. The furnace unit is equipped with four heating elements operating in the infrared range, which are heated chamber of SiC, in which there is a pattern in the form of a powder, placed in a platinum crucible. Weighing accuracy of the instrument is $\pm 0,1\%$, the reproducibility of the weighing - $\pm 0,01\%$. The sensitivity of the scale - $< 7.10\text{ g}$. Temperature accuracy - $\pm 1\text{ }^\circ\text{C}$.

TGA was carried out in the temperature range from 50 to 700 °C at a heating rate of 10 °C/min. Atomic absorption spectroscopy (AAS) was performed on the spectrometer «AAS – 30».

Micrographs of the samples obtained in a transmission electron microscope LEO912 ABOMEGA, 60 - 120 kV accelerating voltage, increasing the 80-500000 h. Phase and structural studies were carried out at room temperature X-ray diffraction of the company «Rigaku» Focusing on the Bragg-Brentano on $\text{CoK } \alpha$ -radiation in a continuous mode. The experimental results were processed by methods of approximation.

3. RESULTS AND DISCUSSION

Using the previously developed methods [8] were obtained metalcarbon nanocomposites based on polyacrylonitrile (PAN) and nickel chloride hexahydrate.

Formation of metalcarbon nanocomposite precursors are in situ. Uniform distribution of the metal in the polymer matrix during the synthesis of the precursor is achieved by processes complexation between nitrile groups of the polymer and the metal compound. In the pyrolysis of PAN is an allocation of a variety of gaseous products [9], among which there are hydrogen, CO, NH₃, and that reduced nickel chloride. Due to the processes of structural and chemical transformations in the matrix of PAN and coagulation of clusters of reduced metal nanoparticles are formed.

Application of electron microscopy was used to establish the structure and morphology nanocomposite Ni / C. Fig. 1 shows the results of transmission electron microscopy (TEM) nanocomposite Ni/C, obtained at 700 °C.

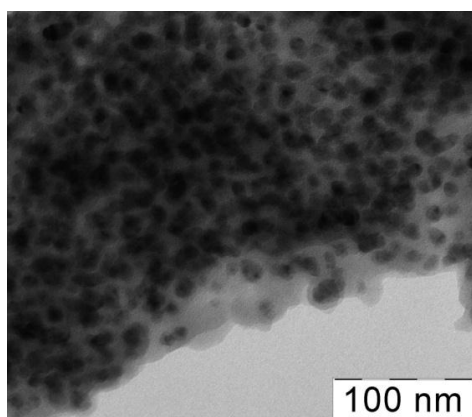


Fig. 1 – TEM of the Ni / C nanocomposite, obtained at 700 °C (Ni / C 700)

Light grey color - the polymer substrate used in the analysis by TEM. Carbon graphite-matrix nanocomposites - dark gray color, which is a layered disordered system with the size of the coherent scattering crystallites L_c from 18 to 37 Å. Studying the structure of the carbon matrix based on PAN was carried out in [10]. Quite dark, black spherical formations - nanoparticles of nickel.

Fig. 2 shows the diffraction pattern of nickel-containing nanocomposites obtained at different temperatures of pyrolysis IR range 400-800 °C.

The diffraction patterns of all the samples in the range of angles 15°-30° fixed amorphous halo, characteristic not strong structured carbon structures. The amorphous halo on radiographs is associated with irregular displacement of graphene planes relative to each other and the small size of the coherent scattering crystallite graphite-like phase [10]. At higher pyrolysis temperatures the formation of ordered carbon structures occurs and at $T = 800$ °C reflection peak corresponding graphite-like carbon phase, the lattice constant of which coincides with a lattice constant of graphite, detected at the diffraction pattern (Fig. 2).

Also the diffraction nanocomposites of scattering angles 2θ of 55° to 101° there are several peaks, which correspond to the angles of reflection of the metal nickel phase (56°; 65.8°; 100.5°).

As a result of TEM calculated distribution of metal nanoparticles in the size of the nanocomposite. The average size of the nanoparticles of the nanocomposite composition of nickel was 15-25 nm, depending on the

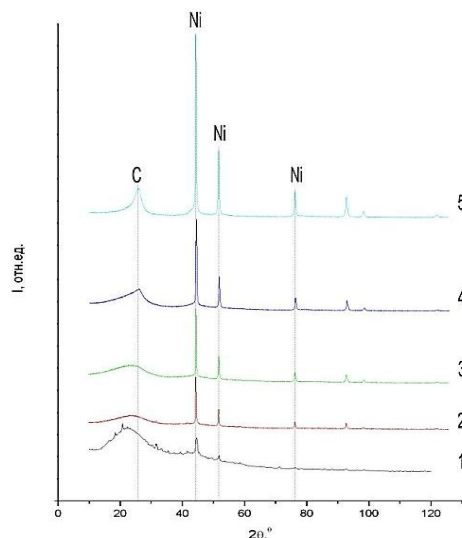


Fig. 2 – Diffraction pattern of the nanocomposite Ni / C: 1) 400 °C; 2) 500 °C; 3) 600 °C; 4) 700 °C; 5) 800 °C

temperature of the process IR-pyrolysis of the precursor. Thus, in the nanocomposites, the obtained at $T = 600$ °C the average size of the nanoparticles was 15 nm and at $T = 700$ °C is advantageously fixed nanoparticles with an average size of 25 nm. The results are shown in Fig. 3. The distribution is in the nature dome-shaped curve in mid-sized metal nanoparticles. With increasing temperature of obtain nanocomposites curve smeared and shifts to larger metal particles.

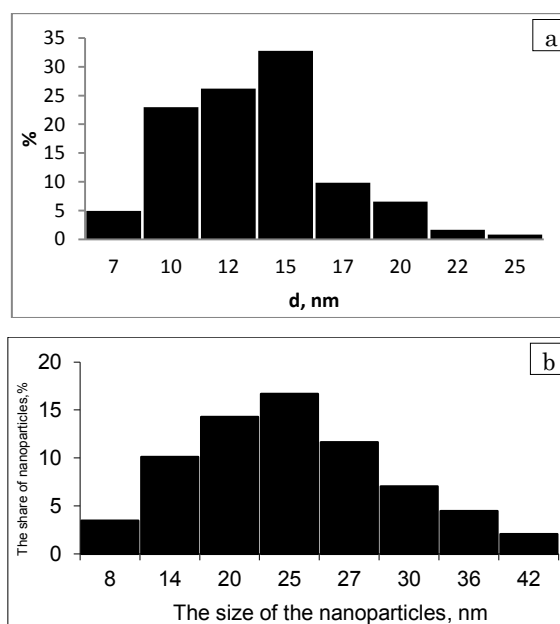


Fig. 3 – The distribution of nanoparticles in size (a) nanocomposite Ni / C, 600 °C; (b) nanocomposite Ni / C, 700 °C; direct measurement of the photographs, obtained using TEM

According to the atomic-absorption spectroscopy (AAC), the nickel content is nanocomposites ~ 15 wt. %, which differs from the originally introduced in the precursor (20 wt. %) and weakly dependent on the temperature of preparation. Apparently, the trend factor caused the formation of volatile metal compounds in the process of degradation of the polymer during the IR-heating.

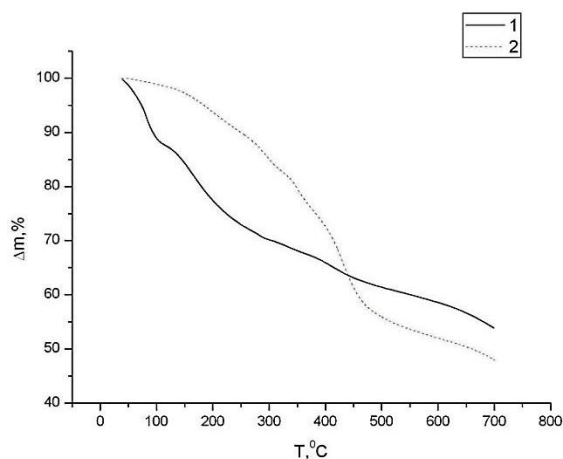


Fig. 6 – The mass change with temperature infrared heating for samples: 1 – $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN with $C_{\text{Ni}} = 10$ wt. %; 2 – PAN

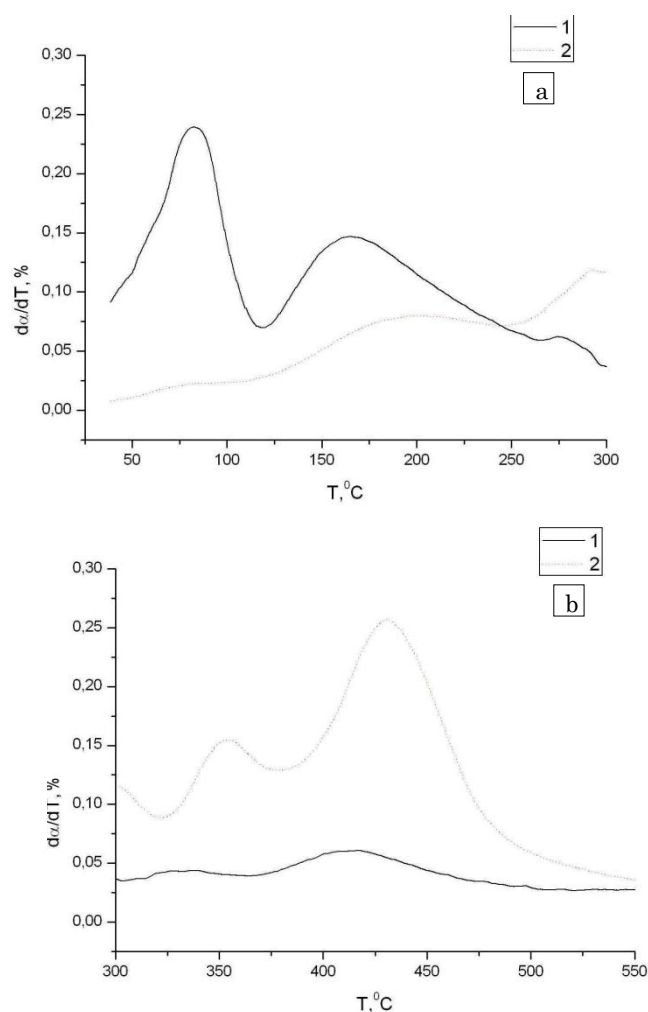


Fig. 7 – The relationship between da/dt and IR-temperature heating: a) from 50 to 300 °C, b) from 300 to 550 °C for samples 1 – $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN with $S_{\text{Ni}} = 10$ wt. %; 2 – PAN

Using thermogravimetric analysis and differential scanning calorimeter processes occurring during IR-heating system $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN have been studied. Fig. 6 shows the change of mass during IR-heating and differential curve (Fig. 7) for the system in $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN compared with the PAN.

Differentiation by the temperature allowed to determine the stage and the temperature ranges for the thermal processes in the synthesis of nanocomposite Ni/C. According to [11] were calculated E_a and k_0 for each step (see Table 2).

Table 1 – Kinetic parameters of the formation of a nanocomposite Ni / C under the influence of IR-heating

Composition sample	$T, ^\circ\text{C}$	$E_a, \text{kJ/mol}$	k_0, min^{-1}
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN $C_{\text{Ni}} = 10$ by mass. %	85	153,2	$1,4 \cdot 10^{14}$
	165	126,0	$1,9 \cdot 10^9$
	330	97,5	$4,2 \cdot 10^7$
	410	17,9	$3,2 \cdot 10^7$
PAN	180	140,2	$2,9 \cdot 10^{14}$
	300	100,8	$4,2 \cdot 10^8$
	350	78,2	$9,2 \cdot 10^7$
	430	27,7	$4,2 \cdot 10^7$

The peaks in the kinetic curves of the composite heating to 300 °C characterize processes of decomposition of the precursor. Differences in the position of the peaks may depend on the characteristics of chemical processes and the degree of drying of the composite. Kinetic curve heating to 300 °C composites $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN includes peaks observed on the kinetic curve heating PAN – 180 and 300 °C. Accordingly, the peaks at 165 °C are allocated to degradation processes PAN. The calculated activation energy for these processes indicates kinetic step ($E_a > 40 \text{ kJ/mol}$) as the limiting (Table 2). Accessory marked peaks in the processes of decomposition of composite components $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN confirm the results of DSC, where the peaks of the most significant changes in the thermal effects corresponding to the endothermic transition to coincide with peaks in the differential TGA curves (Fig. 8).

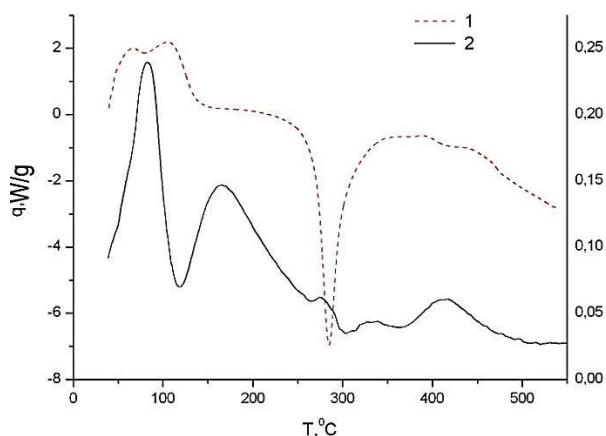


Fig. 8 – Derivatives of conversion of raising the temperature $da/dT(T)$ of composites $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN (1) and the temperature of the heat of reaction $q(T)$ of composites $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / PAN (2)

Comparison of dependences showed that the peaks in the kinetic curves composites heating to 250 °C, we can refer to the processes of dehydration $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and partial destruction of PAN to form a cyclic molecular structure .

4. CONCLUSIONS

Metalcarbon nanocomposites based PAN and nickel chloride hexahydrate were obtained under IR-heating. It is shown that in the system at temperatures IK-PAN / NiCl₂ IR-pyrolysis of 400-800 °C are formed nanocomposites consisting of a carbon matrix and metallic nickel nanoparticles .

According to the results of TGA and DSC nickel in the NiCl₂·6H₂O / PAN causes a decrease in the temperature of the processes of chemical transformations of the polymer matrix, which contributes to the carbonization process. The chemical transformation reactions

the speed limits and not the diffusion of the components. The average size of Ni nanoparticles temperature-dependent production and is 15-25 nm in the range 400-800 °C. Nanoparticle size distribution is asymmetrical nature curve whose maximum is in the average particle size with increasing temperature which the synthesis of nanocomposites is spread and shifts to larger nanoparticles.

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