

HEAT STABILITY OF Me-C NANOCOMPOSITES

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Abstract

The results of investigation of thermal resistance on air of Me-C nanocomposites containing Fe, Ni and Fe-Ni mixtures have been given in the present paper.

Thermal analysis of samples produced by arc-discharge method due to the evaporation of pure graphite and its mechanical mixtures with ferromagnetics (Fe, Ni, Fe-Ni) have been performed using the derivatograph Q-1500D in conditions of dynamic heating from room temperature to 1000°C.

The results of mass change (TG), the rate of mass change (DTG), heat changes (enthalpy change, DTA) for synthesis products during the heating process have been obtained. The results of thermal investigation of products produced by joint evaporation of graphite and ferromagnets, the X-ray phase analysis for graphite samples with ferromagnets before and after oxidation and the temperature dependence of TG, DTG, DTA curves for samples produced by evaporation of pure graphite and mechanical mixtures (C+Fe; C+Ni; C+Fe+Ni) have been presented.

On the basis of the performance of experiments it is necessary to notice that smooth mass decreasing of soot in the low temperature range occurs due to amorphous carbon burning. Under heating till 600°C fullerene-like nanostructures oxidation occurs, and during the following temperature growth the oxidation of graphitized mass proceeds and possible multi-wall carbon nanotubes begins.

The investigations have shown that produced Me-C nanocomposites are oxidized in higher temperature range than the pure soot. Increasing of upper interval of temperature oxidation may be explained by ferromagnetics (catalysts of nanotubes growth) and multiwall nanotubes oxidation. Decreasing of the temperature of oxidation beginning can be explained by formation of amorphous soot-like phase in the samples.

Keywords: fullerite, carbon nanotube, arc evaporation, oxidation, ferromagnet, temperature

1. Introduction

At present time metal carbon nanocomposites have attracted considerable attention due to their unique physicochemical properties. Particular emphasis has been placed on Me-C nanocomposites based on metals of Fe group. The presentation of research results into thermal resistance on air of Me-C nanocomposites containing Fe, Ni and Fe-Ni mixtures has been performed in the present paper.

In the course of tests the method of arc discharge in gaseous phase (ADG) has been used for production of Me-C composites based on iron, nickel and their mechanical mixtures.

This paper describes also the processes occurring in the space between the electric arc and the reactor wall (near electrode area) and on the reactor wall itself.

2. Investigation methods and equipment

The product was synthesized using arc plasma -chemical installation with vertical location of the reactor which had mobile cathode. The mechanical mixture of graphite and metals powders was added into the anode along its axis. Graphite of MPG-7 type was used as material of evaporated cores.

Me-C nanocomposite material was taken out of soot by magnetic separation of parietal soot suspension in hydrocarbons.

As noted before, the charged carbon particles are kept by electromagnetic field of the interelectrode space and practically cannot leave for the near electrode area. Therefore, on consideration of peculiarities of the processes occurring in the gaseous phase and on the reactor walls, their insignificant contribution can be neglected, but account must be taken of the neutral particles.

Relation between the number of neutral and charged particles that are generated by graphite evaporation will depend on the conditions of the performance of the technological process. On the basis of the theoretical analysis and the study of the composition and morphology of the products formed on the reactor walls, the process of nanostructures formation in the gaseous phase and on the reactor walls by arc evaporation of graphite can be represented as the schematic model shown in Fig. 1 [1].

Under the present experimental conditions, in the arc evaporation of graphite the portion of carbon vapor, which consists of neutral particles of plasma stream, moves under the action of both gradients (ΔT and ΔP) from the center of the arc column to the periphery along the arc radius. This carbon vapor escapes the arc area (interelectrode space) at a velocity of more than 20-25 m/s., reaches the reactor wall within 0,003s. and cools down to the room temperature. For this period, a number of processes occur; their duration varies starting from fractions of a nanosecond. The formed products concentrate on the reactor walls and are called "wall soot".

As particles move away from the axis of the electric arc column, their temperature and concentration decrease, their geometrical dimensions increase, the diffusion rate is lowered, so that the number of collisions with other molecules per time unit decreases. Different compounds and structures can be formed under change of energy and the number of carbon reagents collisions in the gaseous phase. The forming fullerenes can transform into onions and into nanotubes and another structures in the presence of a catalyst.

relatively fast, within fractions of a nanosecond. To obtain the product of a specified dispersion, i.e. the material consisting of the particles of certain geometrical dimensions and structure and having certain properties, the duration of interaction needs to be controlled at each level of structure formation.

A nucleus can be constructed from the chains of different lengths and degrees of branching, cycles and polyhedrons. Its frame can be skeleton and the combination of the above-listed structural elements. Increasing number of atoms in the cluster frame (nuclearity) results in the increasing number of methods for their connection. When nuclearity is higher than 20, according to the thermodynamics and geometry the spherical spatial structure is the most favourable; this is observed in the case of fullerene clusters of carbon.

Investigations of micro- and nanostructures of produced composites have been carried out using transmission electron microscope (TEM). The spectrum analysis of extracts of obtained product has been performed by the method of UV-VIS spectroscopy by spectrophotometer SF-2000.

Thermal analysis of samples produced by the arc-discharge method through the evaporation of pure graphite and its mechanical mixtures with ferromagnets (Fe, Ni, Fe-Ni) has been carried out with the derivatograph Q-1500D in conditions of dynamic heating in air from the room temperature to 1000°C.

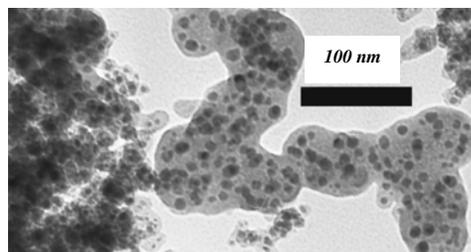
3. Results and discussion

TEM-investigations have shown that Me-C composites consist substantially of metallic particles covered by carbon (Fig. 2, *a*-Ni; *b*-Fe). As is obvious from figure, metallic particles of 1-30 nm in diameter are completely enclosed in multi-layer carbon capsules. These metallic particles have quasi-spherical morphology.

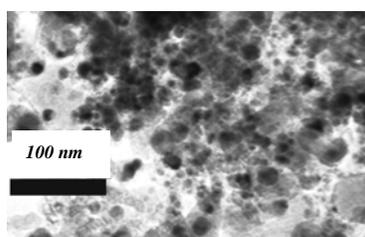
The X-ray investigations have shown that nickel nanoparticles covered by carbon shells are predominantly the monocrystalline metal (of FCC lattice). Iron particles form carbide Fe₃C.

It should be pointed out that by the action of external magnetic field on the suspension of produced Me-C composites their particles move along strength lines of the field. The process of separation of these composite particles is based on this property. The fraction of the very low-mobility contains the composite with encapsulated particles of 5-10 nm in diameter.

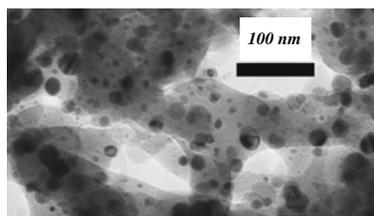
TEM-investigations have been carried out before and after extraction of a component from the synthesis products. Pictures of B.2(X) samples of fullerene-containing soot have engaged one's attention (Fig. 3). The soot particles, encapsulated as thin web of fibrous crystals of 5 nm in diameter, have been clearly seen in Fig. 3, (*a*) after soot washing in ethanol. After the same sample washing in toluene during 5 minutes, the following toluene outlet, and at last filling the system by ethanol, TEM picture has changed slightly (Fig. 3, *b*). The most of the smallest crystals have disappeared, although some of them have stayed. In their instead more large crystals have appeared of length $l = 20-150$ nm and of diameter $d = 5-20$ nm. These appeared fullerite crystals are the products of process of fullerene molecules salting-out by alcohol from toluene solution residue. A well washed insoluble graphite-like nanoparticles remain after the prolonged extraction (Fig. 3, *c*).



(a)



(b)



(c)

Figure 2. Metallic particles of Ni (a), Fe (b) and Fe+Ni (c) covered by carbon film

The same pictures have been observed for Ni-C (B.7), Fe-C (B.5), (Fe+Ni)-C (B.9) samples of composites.

The extracts of B.2(X), B.5(Fe), B.7(Ni) and B.9(Fe+Ni) samples, which contain presumably mixture of fullerenes C_{60} and C_{70} , have been analyzed using electron-absorption UV-VIS-spectroscopy according to the method developed at our department of the Institute for Problems of Materials Science of NASU.

The kinds of the resulting spectrums are given in Fig. 4 and Fig. 5.

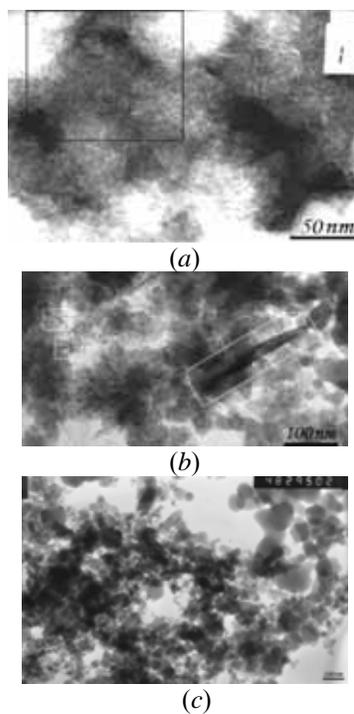


Figure 3. Fullerene-containing soot for the sample B.2(X)

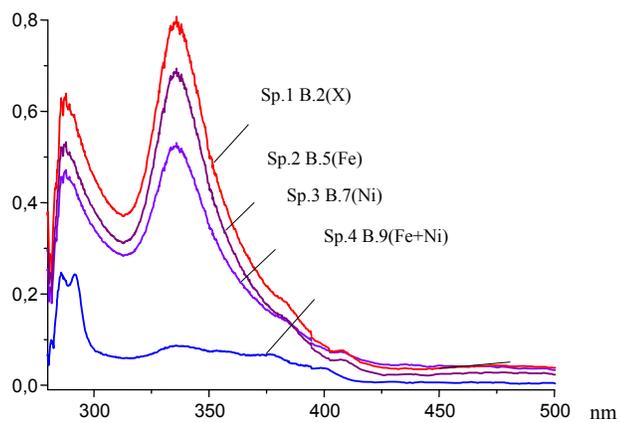


Figure 4. The spectrums of absorption UV-VIS spectroscopy for B.2(X), B.5(Fe), B.7(Ni), B.9(Fe+Ni) extracts

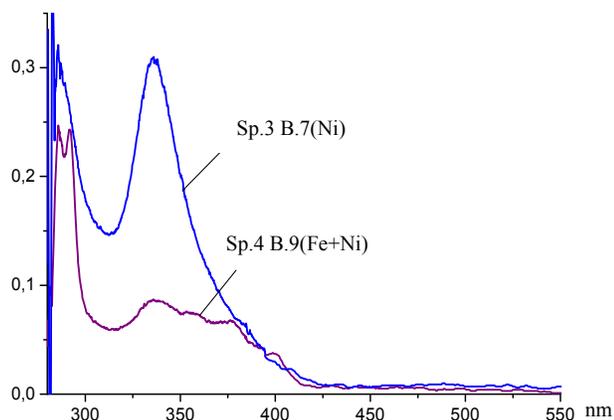


Figure 5. The spectrums of absorption UV-VIS spectroscopy for B.7(Ni) and B.9(Fe+Ni) extracts

Analysis of the spectrums Sp.1 and Sp.2 have shown that B.2(X) and B.5(Fe) extracts respectively have good detected adsorption bands (AB) with $\lambda_{\max} = 287,9$ nm and $\lambda_{\max} = 407,2$ nm corresponding to C_{60} and $\lambda_{\max} = 336,0$ nm and $\lambda_{\max} = 472$ nm corresponding to C_{70} respectively. This clearly demonstrates that both of solutions consist of C_{60} (84%) and C_{70} (16%) mixture.

The spectrum Sp.3 of B.7(Ni) probe solution has good detected absorption bands with $\lambda_{\max} = 287,9$ nm and $\lambda_{\max} = 336$ nm, however, AB at $\lambda_{\max} = 407$ nm (corresponding to C_{60}) and $\lambda_{\max} = 472$ nm (corresponding to C_{70}) are absent in the spectrum. The spectrum Sp.4 determined for probe solution B.9(Fe+Ni) differs strongly from the previous ones. Instead of two AB there are brightly split AB at $\lambda_{\max} = 287,9$ nm and $\lambda_{\max} = 291,9$ nm and three slightly detected AB at $\lambda_{\max} = 335,8$ nm, $\lambda_{\max} = 353,2$ nm, $\lambda_{\max} = 376,1$ nm. These results show that soluble component of synthesis products of composite nanomaterials depends on the chemical composition of precursor. The third soluble component of products of arc evaporation for mechanical mixtures of graphite with various components can be both endo- and exocomponents of fullerenes.

The findings of an investigation into mass change (TG), the rate of mass change (DTG), heat changes (enthalpy change, DTA) for synthesis products in the course of heating are given in Fig. 6 and Table 1.

The results of X-ray phase analysis for the samples before and after oxidation, which have been received using the diffractometer DRON-3M, are represented in the Table 2.

The investigation which have been carried out show that oxidation of graphitized parietal soot occurs in the temperature range 329-778°C. The broad asymmetric peak with $T_{\max} = 684^{\circ}\text{C}$ corresponds to this process on the DTG curve. The DTG curve nature in the temperature range ~500-665°C points to the formation of a number of nanostructures with various thermal resistance. The moderate broad exothermic peak is noticed in this temperature range on the DTA curve. It overlaps with more large exothermic peak with the maximum intensity at 709°C (Fig. 6, a; Table 1 and Table 2).

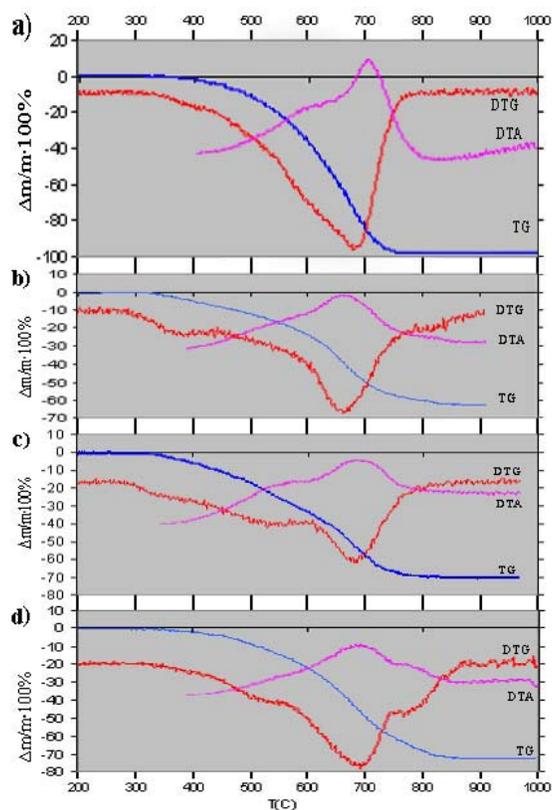


Figure 6. The temperature dependence of TG, DTG, DTA curves for samples produced by evaporation of pure graphite (a) and mechanical mixtures C+Fe (b); C+Ni (c); C+Fe+Ni (d)

Table 1. The results of thermal investigation of products produced by joint evaporation of graphite and ferromagnets

№	Material	Temperature range of oxidation, °C	Mass Decrease %	DTG				DTA
				T _{1shoulder} °C	T _{2shoulder} °C	T _{1max} °C	T _{2max} °C	
1.	C _(soot)	329-778	98			684		709
2.	C+Fe	209-886	61	386		668		668
3.	C+Ni	209-849	70.4	346	530	683		692
4.	C+Fe+Ni	206-894	72.3		505	690.5	776	697

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It has been known from literature data that amorphous carbon burns up in the temperature range 300-500°C. Fullerenes inflame at 550°C. The oxidation temperatures of one-wall and multi-wall carbon nanotubes equal 650 and 750°C respectively. The graphitized particles interaction with air oxygen occurs at ~800°C [4, 5].

On the basis of obtained data it should be mentioned that the smooth decreasing of soot mass in the low temperature range occurs due to amorphous carbon burning. The oxidation of fullerene-like nanostructures, on heating till 600°C, occurs and as the temperature increases later on the oxidation of graphitized mass and possible of multi-wall carbon nanotubes begins.

Table 2. The results of X-ray phase analysis for graphite samples with ferromagnets before and after oxidation.

№	Material	Phase composition before oxidation	Phase composition after oxidation
1.	C _(soot)	rombohedral distortion of graphite	—
2.	C+Fe	Soot (amorphous phase, halo on $2\theta \approx 12-22^\circ$), graphite traces, (line of intermediate intensity, $d=3,36\text{Å}$), α -Fe (VCC) and γ -Fe FCC- lattices	Main phase – Fe ₂ O ₃ , amorphous phase, (halo on $2\theta \approx 14-24^\circ$)
3.	C+Ni	Soot Ni(C)- solid solution(interplanar spacing are increased), traces of NiC.	Main phase – NiO, amorphous phase, (halo on $2\theta \approx 16-25^\circ$)
4.	C+Fe+Ni	Fe _{0,64} Ni _{0,36} (cubic crystal system), soot, traces of graphite with rombohedral distortion	Main phase – Ni _{1,43} Fe _{1,7} O ₄ (FCC), NiO, amorphous phase, (halo on $2\theta \approx 12-24^\circ$)

The products containing ferromagnetics begin to oxidize at lower temperatures (206-209°C) and this process takes place in broader temperature range. The decrease of the product masses constitutes 61-72,3% (Fig. 6, b-d; Table 1, p.p.2-4). Under oxidation of the product containing Fe the shoulder is observed on the DTG curve at temperature about 386°C and large asymmetric peak is seen at $T_{1\max} = 668^\circ\text{C}$ (Fig. 6, b; Table 1, p.2). The DTG curve of oxidation for the product with Ni in parallel with the low temperature shoulder at $T_{1\text{shoulder}} = 346^\circ\text{C}$ (Table 1, p.3) contains the second shoulder at $T_{2\text{shoulder}} = 530^\circ\text{C}$. Temperature of the large asymmetric peak equals $T_{1\max} = 683^\circ\text{C}$ as in the case of oxidation of the product with Fe (Fig. 6, c; Table 1, p.3). The shoulder presence at 505°C only (Table 1, p.4) the displacement of the large asymmetric peak to higher temperature range (690°C), the appearance of one more little peak at 776°C (Fig. 6, d; Table 1, p.4) are special features of high temperature behavior for the product containing Fe-Ni.

Under oxidation of the samples with ferromagnets the occurrence of shoulders on the DTG curves at 346 and 386°C is evidently associated with the burning of amorphous carbon. More intricate character of TG, DTG, DTA curves of these samples oxidation (in comparison with pure soot) at higher temperatures is associated with formation of solid products during heating due to the metal oxidation at temperatures above 300°C. According to the X-ray phase analysis oxides

Fe₂O₃, NiO, complex oxide Ni_{1.43}Fe_{1.7}O₄, amorphous halo at 2 θ ≈12-24° (Table 2) are found in the residue of the samples that have been oxidized.

The appearance of wide peak (T_{max}=668 – 690°C) (Fig. 6,b-d; Table 1, p.p.2-4) on the DTG curve as in the case of soot oxidation points to the availability of carbon nanotubes in products with ferromagnets.

4. Conclusions

The conventional schematic model of carbon nanostructures formation at the arc evaporation of graphite in gaseous (neutral) phase has been suggested. The basis for this model is the behaviour of particles in electromagnetic field at the extremely high gradients of pressure and temperature on an arc radius.

One of the most important conclusions following from the experimental observations can be considered the fact that all micro- and macrovolumes of carbon nanomaterials are formed at the stage of nucleation, i.e. a nanostructural product consists of nuclei of different structures.

The Me-C nanocomposites (where Me = Fe, Ni, Fe+Ni) have been produced and they have structures like the nucleus-cover.

It has been noticed the response of nanocomposites to the magnetic field action.

The initial fullerite crystals, which are contained in soot before extraction process, have been shown.

The self-descriptiveness and the high of the speed performance method developed by these authors of the qualitative and quantitative analysis of the soluble nanomaterials have been noted.

The carried out investigations have shown that produced Me-C nanocomposites are oxidized in a wider temperature range than the pure soot. Increasing of upper interval of temperature oxidation can be explained by oxidation of ferromagnets (catalysts of nanotubes growth) and multiwall nanotubes. Decreasing of the temperature of oxidation beginning can be attributed to the formation of amorphous soot-liked phase in the samples being studied.

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