

Carbon coated nickel nanoparticles produced in high-frequency arc plasma at ambient pressure



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ABSTRACT

The nickel particles with the mean size about 10–20 nm coated with carbon were extracted by the treatment of the carbon condensate with nitric and hydrochloric acids. The initial carbon condensate containing nickel nanoparticles with a graphite conversion was synthesized in the high-frequency carbon-helium arc plasma at ambient pressure with the nickel nanoparticles as a catalyst. The nickel content in the nanoparticles was 84.6 wt %. Magnetic properties of the nanoparticles are characterized by the high hysteresis and thermal stability. The sample of compacted nanoparticles is characterized by electrical resistance much higher than it in of compacted initial condensate.

1. Introduction

As shown by numerous studies, material properties depend on the characteristic size of the particles of crystallites etc. demonstrates new and unique properties. For ferromagnetic materials this value is the size of a single-domain structure, and for the non-magnetic metal particles – the electron mean free path. With decreasing particle size or crystallite the electronic structure of substance is changed [1]. Experimental data for the magnetic nanoparticles with carbon shell can be used to understand the dynamic processes that occur in these materials. This paper presents the results of the study material composed of metal nanoparticles coated with carbon. The material was obtained by the introduction of metallic nickel powder into the stream of carbon-helium plasma, and then recovered with hydrochloric and nitric acids.

The main for synthesis nanoparticles is sputtering of electrodes in a dc arc in the helium atmosphere at the pressure 10–26 kPa. The drawback of this method is impossibility of controlling the synthesis parameters. Overly large or small currents and pressure (outside the mentioned range) usually lead to significant decrease nanoparticles content. The method of the synthesis in HF-arc plasma allows effective obtainment of nanostructures in wider synthesis parameter ranges [2].

2. Experimental method

In this work, we extracted and investigated the components of the condensate produced by cooling the plasma consisting of carbon, nickel, and helium. Plasma was formed in a high frequency arc at atmospheric pressure [3]. This setup can be used for obtaining carbon condensate with different dispersion and structure, as well as containing nanoparticles and endohedral metallofullerenes. The arc was ignited between two graphite rods 6 mm in diameter located an angle 54° between electrodes. Finely mixture of nickel powder with a particle size of 0.25 μm and graphite powder was placed in an axial hole of the graphite rod electrodes. The ratio of the nickel introduced into the plasma to carbon was 36 wt%.

Synthesis was carried out under 66.5 kPa helium pressure at chamber. The arc was fed by an electric current of 220 A at a frequency of 66 kHz, which made it possible to transform almost all electrode material (98%) into a condensate formed on the walls of the water cooled chamber. From the condensate (sample 1) collected off the chamber walls was extracted fullerene at Soxhlet apparatus using toluene as solvent. It was boiling at a temperature of 90 °C in a strong nitric acid for 3.5 h. The precipitate filtered through an FS-III paper filter was insoluble in the acid and amounted to 76 wt% of the initial condensate. It was washed in distilled water to remove the acid and salt

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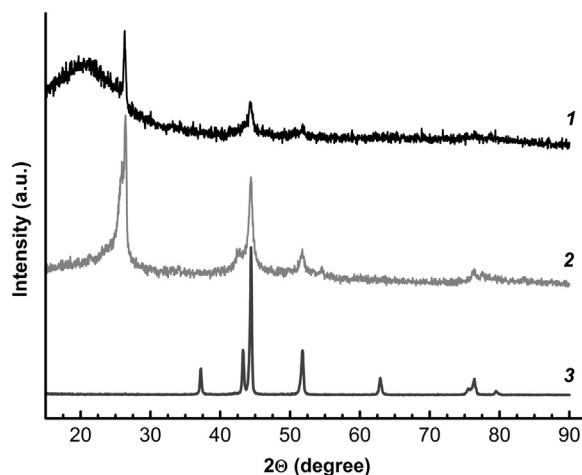


Fig. 1. X-ray diffraction patterns of samples 1 (1), sample 2 (2) and sample 3 (3).

products and then was dried under normal conditions (sample 2).

The solution, which was obtained upon boiling carbon black in the acid, was evaporated; then, the residue was washed in distilled water at a temperature of 60 °C until the solution reached the pH value of 5. The precipitate thus obtained was dissolved in a dilute hydrochloric acid at a temperature of 90 °C and then was filtered off. The undissolved residue again was washed in distilled water and dried (sample 3) [4]. This method may be also used for fictionalization of fullerene and endohedral metal fullerenes [5].

The structure and composition of the samples were investigated using X-ray powder diffraction (DRON-4 diffractometer), magnetometric measurements (VSM magnetometer), and TEM images (Hitachi HT7700).

3. Results and discussion

The X-ray fluorescence analysis of samples 1–3 has demonstrated that the samples contain nickel, carbon and oxygen 22.7, 67.7 and 9.6 wt% for sample 1, 16.4, 56.9 and 26.7 wt% for sample 2 and 84.6, 9.7 and 5.7 wt% for sample 3, accordingly. The X-ray powder diffraction patterns of samples 1–3 contain reflections from graphite (26.4°, 42.6° and 54.5°), nickel (44.3°, 51.7° and 76.4°) and Ni oxide (37.2°, 43.3°, 62.9°, 75.5° and 79.5°) (Fig. 1). The reflection observed at 25.8° in the X-ray powder diffraction pattern of sample 2 corresponds to a graphite structure with an interlayer spacing of 3.42 Å. This reflection is revealed after the removal of finely dispersed carbon from the condensate. The X-ray powder diffraction pattern of sample 1 in the angle range 10–30° contains a halo associated with the amorphous part of the sample, which disappears after the sample is treated with nitric acid (sample 2).

Table 1
Resistivity of carbon condensates before and after processing.

Sample	ΔL (cm)	D (cm)	R (Ohm)	ρ , (Ohm cm)
Sample 1	0.47	0.61	$20 \cdot 10^3$	$12 \cdot 10^3$
Sample 3	0.28		680	709
Sample 2	0.74		28	11

Examination of the samples by transmission electron microscopy showed that the sample 2 is in the nickel particles with a size of several tens of nanometers with a multilayer coating carbon and part of carbon is graphene layers (Fig. 2a). In sample 3, nickel is in the particles with sizes from about 10 and 20 nm (Fig. 2b). The average particles size was estimated with the help of TEM images and was 27 ± 11 nm for sample 2 and 18 ± 8 nm for sample 3.

The resistance of these samples was measured. The sample was poured in a glass tube and pressed between two metal contacts. Resistance was calculated $\rho = RS/\Delta L$, the results are presented in Table 1.

3.1. Magnetic properties

Magnetic measurements were made by vibrating sample magnetometer VSM in the temperatures from 80 K to 300 K. The powder sample was weighted and then fixed in wax matrix to avoid particle displacement in VSM cell. There is significant magnetic hysteresis that decreased slightly with temperature increasing in the studied powders (Fig. 3a,b). The magnetic hysteresis observation implies that the blocking temperature in Ni nanoparticles is higher than the upper limit of the temperature range used in our measurements (300 K). The particle sizes in our Ni nanoparticles are less than the equilibrium single domain particle size for Ni (according to Ref. [6,7] it is in the range 40–80 nm). The coercive force in the sample 2 (see Table 2) is close to the magneto-crystalline field in fcc Ni at room temperature $H_a^{Ni} = 2K/M_s = 180$ Oe [8]. It also indicates the particle size of the proximity to the size of the single-domain size.

The decay in coercive force and remnant magnetization, according to the Table 2, can be estimated as 0.20% per Kelvin and 0.13% per Kelvin respectively for the sample 2% and 0.20% per Kelvin and 0.17% per Kelvin for the sample 3. These small decays of magnetic properties can be regarded as thermo-stability for the magnetic applications of the synthesized powders.

The saturation magnetization in the samples 2 and 3 are 4.3 emu/g and 27.2 emu/g respectively. We use it to estimate the volume fraction of pure Ni in the samples. Taking the saturation magnetization for pure Ni 59 emu/g we obtain the volume fraction of pure Ni is 7 wt% in the sample 2 and 46 wt% in the sample 3. These weight fractions of Ni are less than that measured by X-ray fluorescence. This is due to the part of the nickel atoms is not composed of ferromagnetic phases. A non-

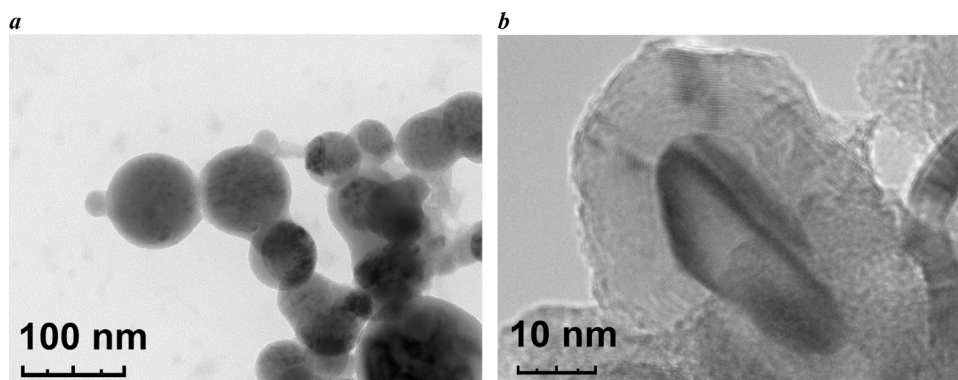


Fig. 2. TEM images of sample 2 (a) and sample 3 (b).

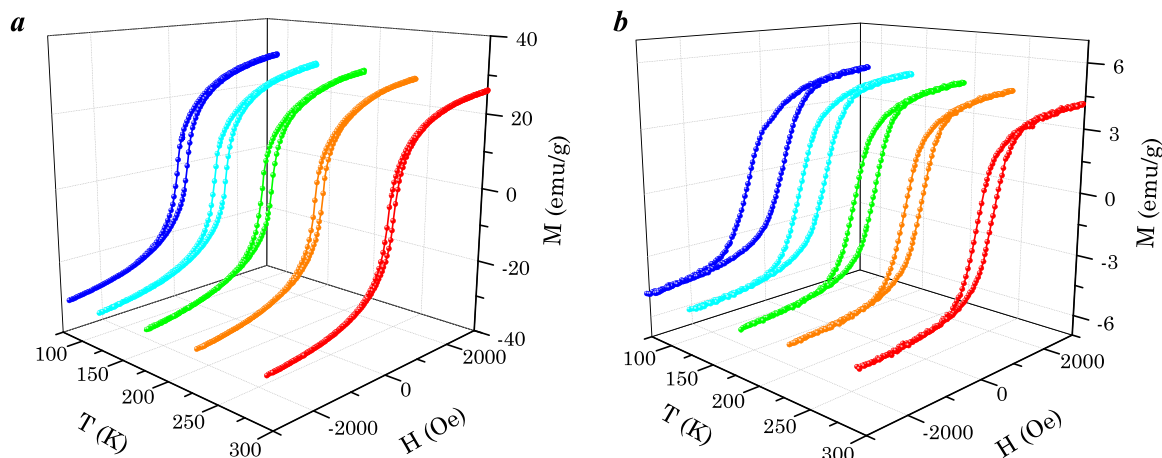


Fig. 3. Hysteresis loops for Sample 3 (a) and Sample 2(b) (automated vibrating magnetometer with Puzey electromagnet).

Table 2
Magnetic properties of Ni@C.

Sample	T (K)	Hc (Oe)	Mr (emu/g)	Ms (emu/g)
Sample 2	90	390	2.3	4.9
	300	200	1.6	4.3
Sample 3	90	150	9.1	31.8
	300	79	5.7	27.2

magnetic phase (phase with negligible magnetization) included nickel atoms is the nickel monoxide observed in the X-ray diffraction pattern of the sample 3. The nickel monoxide is antiferromagnetic in the bulk but in nanoparticles it can behave as a spin-glass. In both cases, the nickel atoms in the composition of these phases will not contribute to the value of the saturation magnetization. In both cases, the nickel atoms of these phases will not contribute to the saturation magnetization. Additionally thin layers of Ni₃C may be formed at the boundary of carbon and nickel. The phase Ni₃C is hard to be resolved in X-ray diffraction pattern due to overlap of the most intensive peak (113) in Ni₃C pattern with the huge one (111) peak from fcc Ni. The Ni₃C phase is considered in recent papers as an inevitable product of the catalytic growth of graphene layers on the nickel nanoparticles [9]. The presence of Ni₃C phase with very low magnetization [10] may be the explanation of discrepancy between Ni weight fraction estimated from saturation magnetization and from X-ray fluorescence data.

4. Conclusions

It was shown that in the carbon-helium plasma with nickel used as a catalyst, we obtained a carbon condensate containing nickel nanoparticles with a graphite conversion. Sequential treatment with nitric and hydrochloric acids made it possible to extract nickel particles coated with carbon. The nickel content in these particles was 84.6 wt%. The particle size does not exceed 18 ± 8 nm. Nanostructured composite ferromagnetic materials had different thermal stability and high

resistance.

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