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SYNTHESIS AND CHARACTERIZATION OF CARBON-COATED $Ni_{1-x}Cu_x$ FERROMAGNETIC NANOPARTICLES FOR SELF-REGULATING MAGNETIC HYPERTHERMIA

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Abstract–Using the solid-state pyrolysis of metal-phthalocyanines (NiPc and CuPc), carbon-coated ferromagnetic $Ni_{1-x}Cu_x$ $(0 < x < 0.5)$ nanoparticles have been synthesized. The structure, composition and morphology of samples were investigated by means of scanning electron microscopy, energy-dispersive X-ray analysis, and powder X-ray diffraction. It is shown that the mean sizes of nanoparticles are varied from 30–40 nm to 350–400 nm depending on the pyrolysis conditions, and the thickness of carbon coating is about 10–20 nm. From X-band ferromagnetic resonance spectra it is obtained that the Curie temperature of nanoalloys can be varied in a wide range (from –150°C to 60°C) depending on the concentration of diamagnetic Cu atoms. The prepared samples can be used for self-regulating magnetic hyperthermia in oncology.

1. Introduction

Recently there has been continuously grown interest in ferromagnetic nanoparticles both from the physical point of view and for many applications (see, e.g., [1,2]). In particular, such materials are used in various fields of medicine: as magnetic contrast agents in magnetic resonance imaging, for drug delivery, magnetic separation of cells, etc. Magnetic nanoparticles with a temperature of the ferromagnet–paramagnet phase transition (Curie temperature T_C) in the range of 42–46°C are of particular interest, because they can be used in oncology for self-regulating magnetic hyperthermia. Such particles can provide a local self-regulating heating of cancer cells by a.c. electromagnetic field (without damage of healthy tissues), since above T_C magnetic nanoparticles become paramagnetic and lose the ability of heating by the external electromagnetic field.

One of materials with an appropriate Curie temperature are $Ni_{1-x}Cu_x$ binary alloys, where one can obtain a needed temperature of magnetic transition by changing the concentration x of diamagnetic Cu atoms [3]. Previously $Ni_{1-x}Cu_x$ nanoparticles have been studied in [4-6], where the mechanical alloying and chemical methods were used for preparation of nanoalloys. Note that the nanoparticles for magnetic hyperthermia should possess a number of other properties: biocompatibility, non-toxicity, stability and, in addition, their sizes should not exceed the sizes of blood capillaries (about 400 nm).

In this paper, we propose a relatively simple method for preparation of carbon-coated $Ni_{1-x}Cu_x$ ferromagnetic nanoparticles for magnetic hyperthermia with required properties. Using ferromagnetic resonance measurements, the Curie temperatures of prepared nanoparticles were determined.

2. Experimental Technique

For preparation of nanoalloys we used the polycrystalline powders of metal-phthalocyanines $\mathrm{MPc} \equiv \mathrm{M(C_{32}H_{16}N_8)}$, where $\mathrm{M = Ni,\ Cu}$. The solid-phase pyrolysis can be represented by the following reaction [7-9]:

$$\left(\mathrm{NiPc}\right)_{1\text{-x}}(\mathrm{CuPc})_{\mathrm{x}} \xrightarrow[-8\mathrm{H_2},\,-4\mathrm{N_2}]{T_{\mathrm{P}},\,t_{\mathrm{P}}} (\mathrm{Ni_{1\text{-x}}Cu_x}) + 32\mathrm{C},$$

where T_{p} is the pyrolysis temperature (600–1000°C) and t_{p} is the pyrolysis time (15–300 min). We have prepared the nanoalloys with the concentration of diamagnetic Cu atoms from 0 to 50 at% $(0 < x < 50)$. The pyrolysis process was performed in a closed ampoule at vacuum.

The composition, morphology and sizes of synthesized samples were investigated using scanning electron microscope (SEM) Vega Tescan 513 MM and energy-dispersive X-ray (EDX) spectrometer INCA Energy 300. The structure of nanocomposites was studied with an X-ray diffractometer DRON-3 (radiation $\mathrm{CoK_{\alpha}}$). Magnetic properties of nanoalloys were studied with an X-band ESR spectrometer in the temperature range of 77–350 K.

3. Results and Discussion

For pyrolysis of metal-phthalocyanines the polycrystalline powders of NiPc and CuPc were mixed, taking into account the required value of x. A number of samples with different values of x were synthesized at the pyrolysis temperatures from 600 to 1000°C. It follows from SEM images that the prepared powders consist of carbon plates (with the mean sizes of 30–40 μm) containing the metallic nanoparticles. It is essential that the mean size of nanoparticles depend on the temperature and time of pyrolysis: it can be varied from 30–40 nm up to 350–400 nm. This is clearly seen for samples presented in Figs.1 and 2, where the bright spots correspond to metallic nanoparticles embedded in a dark carbon matrix.

The analysis of EDX data shows that the obtained nanoparticles are sufficiently homogeneous in composition and the value of x in them corresponds to the preliminary chosen Ni:Cu ratio.

In X-ray diffraction spectrum of $\mathrm{Ni}_{1-x}\mathrm{Cu}_x$/C nanocomposites (Fig.3) one can see a broad peak at $2\theta \approx 30°$, corresponding to graphitic coatings around nanoparticles, and 3 narrow peaks at $\approx 50°$, 58°, and 89° related to Ni-Cu nanoalloy with a fcc crystal structure.

Figure 4 presents the ferromagnetic resonance spectra of $\mathrm{Ni_{0.7}Cu_{0.3}}$ nanoparticles in carbon matrix at 77 K and 300 K. The obtained value of g-factor is equal to $g = 2.23$ with the linewidth $\Delta H \approx 750$ Oe. The intensity of signal at 300 K is considerably lower, which is caused by the proximity of the Curie temperature.

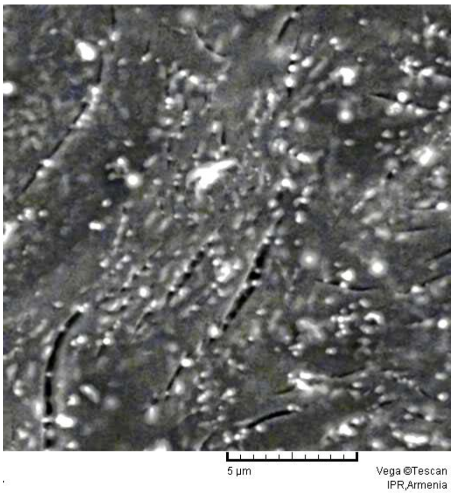

Fig.1. SEM image of a $Ni_{0.7}Cu_{0.3}$/C sample prepared at T_p = 700°C, t_p = 30 min.

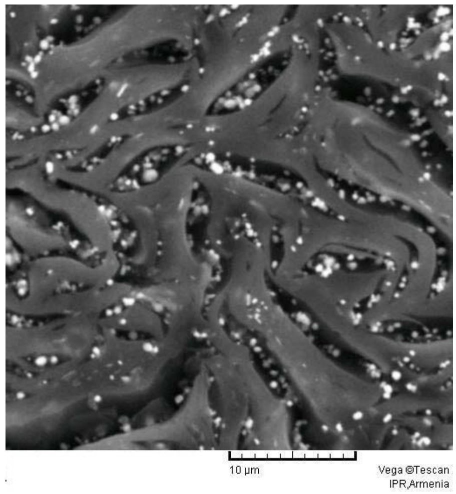

Fig.2. SEM image of a $Ni_{0.8}Cu_{0.2}$/C sample prepared at T_p = 900°C, t_p =30 min.

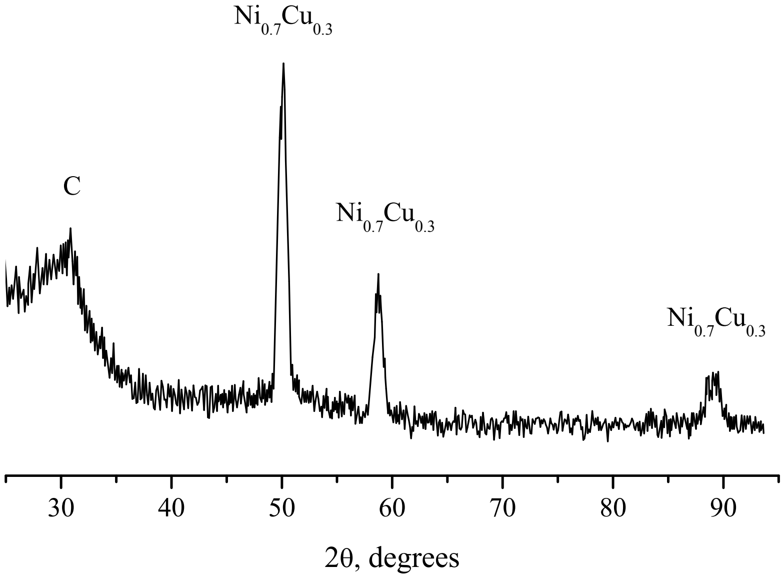

Fig.3. X-ray diffraction spectrum of $Ni_{0.7}Cu_{0.3}$/C nanocomposite prepared at T_p = 700°C, t_p = 30 min. Radiation CoK_α, λ = 1.790 Å.

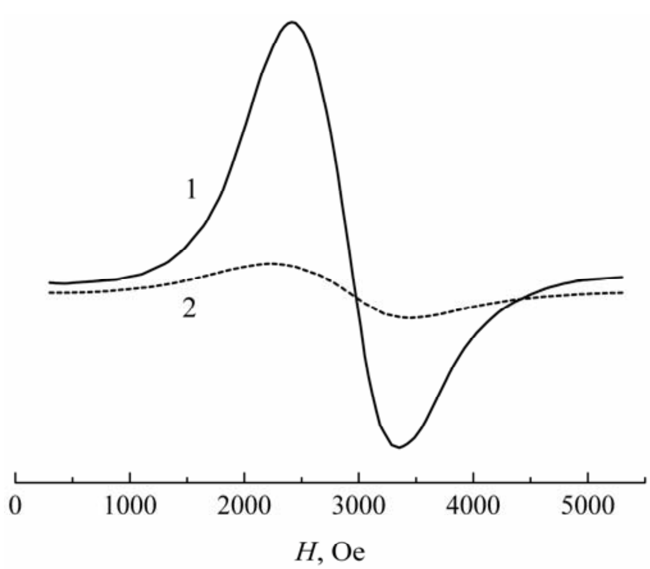

Fig.4. Ferromagnetic resonance spectra of $Ni_{0.7}Cu_{0.3}$ nanoparticles in carbon matrix at 77 K (1) and 300 K (2).

Using ferromagnetic resonance measurements, the Curie temperatures of prepared nanoparticles were determined (Fig.5). It is essential that within the limits of experimental errors these data coincide with the dependence $T_C(x)$ for bulk $Ni_{1-x}Cu_x$ alloys [3]. Note that the value of T_C required for hyperthermia corresponds to $x \approx 0.3$.

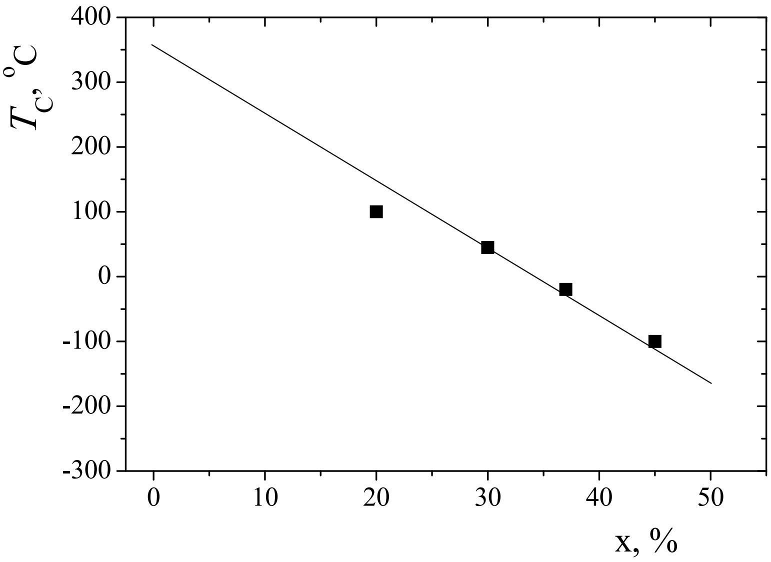

Fig.5. Dependence of the Curie temperature of carbon-coated $Ni_{1-x}Cu_x$ nanoalloys on the concentration of diamagnetic Cu atoms. Solid line corresponds to data for bulk alloys from [3].

It should be noted that owing to the carbon coating the prepared nanoparticles are stable in ambient conditions and the oxidation processes are absent. It is also of importance that the carbon matrix is biocompatible and prevents the aggregation of nanoparticles. We believe that after the corresponding grinding and magnetic separation the prepared nanoparticles may be used for self-regulating magnetic hyperthermia.

4. Conclusion

Thus, using solid-state pyrolysis of metal-phthalocyanines, we have synthesized and investigated the ferromagnetic Ni-Cu nanoalloys in carbon matrix. It is shown that the size of metallic nanoparticles depends on the pyrolysis conditions and can be varied in a wide range. The Curie temperature of nanoalloys strongly depends on the concentration of diamagnetic Cu atoms, which makes them feasible for self-regulating magnetic hyperthermia.

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