Аннотация к статье

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Fe$_{45}$Ni$_{55}$ Magnetic Nanoparticles Obtained by Electric Explosion of Wire for the Development of Functional Composites

Магнитные наночастицы Fe$_{45}$Ni$_{55}$ были синтезированы методом электрического взрыва проволоки. С их использованием были приготовлены наполненные магнитополимерные композиты на основе сополимера БМК-5, содержащего 95% звеньев бутилакрилата и 5% звеньев метакриловой кислоты. Магнитополимерные композиты являются перспективными для приложений, связанных с микроволновыми свойствами. Различными физическими и термодинамическими методами были исследованы структура, магнитные свойства композитов и межфазное взаимодействие наночастиц FeNi с полимерной матрицей.

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Nanomagnetics _____

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Abstract— Fe$_{45}$Ni$_{55}$ nanoparticles (MNPs) were obtained by the electric explosion of wire technique. FeNi MNPs/ copolymer of 95 wt% butylacrylate and 5wt% methacrylic acid composites in the range of 5 to 90 wt% of MNPs were prepared with focus on their microwave applications. Interaction between MNPs and polymeric matrix, structure, magnetic properties of the MNPs and the composites were studied by different techniques.

Index Terms— Nanomagnetics, FeNi Magnetic nanoparticles, polymer/nanoparticles composites, microwave absorption

I. INTRODUCTION

Among others FeNi MNPs were intensively studied in a view of their electronics and microwave applications [Gangopadhyay, 1992]. One of the factors limiting MNPs utilization is a small size of the batch. Electric explosion of the wire (EEW) is an electrophysical method based on the evaporation of metal wire by the electric high power pulse in the inert atmosphere. It yields essentially spherical MNPs and production rates up to 200 g/h [Kotov 2003]. We describe our experience on fabrication and characterization of EEW FeNi MNPs and MNPs/polymer composites with focus on microwave applications.

II. EXPERIMENTAL

A. Synthesis of MNPs

FeNi MNPs were synthesized by the EEW using FeNi wire with 0.5 mm diameter in a reaction chamber filled with a circulating mixture of 70% of Ar and 30% of N$_2$ providing the gas pressure of 0.12 MPa. Controlled quantities of oxygen about 0.02 g per gram of MNPs were slowly injected into the chamber in order to reduce their agglomeration and pyrophoricity by the formation of about 2-6 nm oxide surface barrier layer.

B. Structural characterization of MNPs

Transmission electron microscopy (TEM) was performed by a JEOL JEM2100 microscope operating at 200 kV. Fig. 1 shows TEM image of representative MNPs ensemble. MNPs are spherical. Particle size distribution (PSD) was obtained by the analysis of 540 particle images.

PSD is fitted well by the following number average lognormal distribution function:

$$P_n(d) = \frac{397.2}{d} \exp\left\{-\frac{1}{2}\left(\frac{\ln d - \ln(41.0)}{0.4943}\right)^2\right\} \quad (1)$$
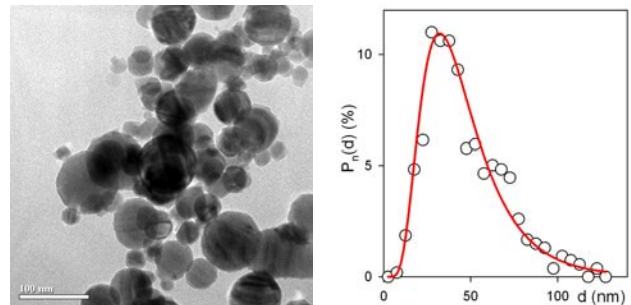

Fig. 1 (a) TEM image of FeNi MNPs. (b) Number average particle size distribution.

The number average diameter of FeNi MNPs calculated using PSD is d$_n$= 45.8 nm. The specific surface area S$_{sp}$ = 11.5 m^2/g. of the FeNi MNPs was measured via Brunauer-Emmett-Teller(BET) technique [ ] by the low-temperature physical adsorption of molecular nitrogen using Micromeritics TriStar 3000 analyser. As FeNi MNPs were spherical, S$_{sp}$ values can be used for the calculation of weighted average diameter (d$_w$) of MNPs according to the equation [X]:

$$d_w = \frac{6}{\rho S_{sp}} \quad (2),$$

where ρ is the density of FeNi MNPs (8.35 g/cm^3). Eq. (2) yielded the value 62 ± 5 nm for MNPs. The average MNPs diameter calculated using PSD parameters (Eq. (1)) was 69.5 nm in a good agreement with adsorption results.

X-ray diffraction study was performed using the DISCOVER D8 (Bruker) diffractometer operating at 40kV, 40 mA with Cu-Kα radiation (λ = 1.5418 Å). The crystalline structure corresponded to the solid solution of Fe in the face-centered cubical lattice of Ni with a = 3.584 Å. The average size of coherent diffraction domains estimated using the Scherrer approach was about 43 nm, close to the number average diameter calculated using PSD.

C. Preparation and characterization of MNP/polymer composites

Magnetic composites were prepared using commercial acrylic copolymer BMA-5 consisting of 95% (by weight) butylacrylate and 5% methacrylic acid. Molecular weight of BMA-5 was 3.2×10^5 according to Mark-Houwink-Sacurada equation: $M = 0.63\times10^{-8}D^{-0.5}$. Diffusion coefficient D of BMA-5 macromolecules in isopropanole was determined by dynamic light scattering (DLS) using Brookhaven ZetaPlus analyzer. Glass transition temperature determined by differential scanning calorimetry (SETARAM DSC131, scanning rate 5 K/min) was 43°C. The MNP/BMA-5 composites were made by casting. First 25% stock solution of BMA-5 in ethylacetate was prepared. Full homogenization was established after 48 hours of mixing at 500 ^{o}C. Suspension of FeNi MNPs (50%) was prepared separately and de-aggregated via ultra-sound treatment for 15 min by Cole-Palmer CPX-750 processor operated at 300 W output. MNPs suspension was mixed with the stock solution of BMA-5 in proportions providing certain MNPs/polymer ratio in final mixed suspension de-aggregation of FeNi MNPs in mixed suspension was done using DISPERMAT TU (VMA-Getzmann) dissolver operated at 3000 rpm for 30 min being monitored by DLS: d_w of MNPs in de-aggregated mixed suspension calculated using PSD parameters was close to the 82 nm value. Then suspensions with certain MNPs/BMA-5 ratio were cast onto glass surface and dried at ambient conditions. Thus, MNPs/polymer compositions, in the range of 5 to 90 wt% of MNPs were prepared. Compositions with up to 70% of MNPs content were solid films, with 80 and 90% of MNPs they were flakes.

Distribution of MNPs in composite films was studied by scanning electron microscopy (SEM) using JEOL JSM-7000F. The preparation included sputtering deposition of 20 nm carbon layer upon the surface of the composite in order to avoid charge effects.

Interaction of polymer with the surface of FeNi MNPs embedded in the composite matrix was measured via thermochemical cycle [Safronov2012] The enthalpies of the processes incorporated in the thermochemical cycle were measured in isothermal conditions at 25 ^{o}C using Calvet 3D calorimeter SETARAM C80. Typically measured heat effects fell within 0.1 – 5 J range, depended on the load. The relative error of measurements of the heats of dissolution and the heats of wetting was estimated as 5% for the heat effects ranging from 0.1 to 0.5 J and 2% for the heat effects in the 0.5 – 5 J range.

Magnetic properties were measured at room temperature using a vibrating magnetometer Cryogenics Ltd. London W3

7QE, UK) in a magnetic field up to 18 kOe.MNPs were measured in gelatin capsule. For composite small piece of the film was measured in the film plane. Ferromagnetic resonance (FMR) measurements at 9.5 GHz were carried out on an ELEXSYS 500 Bruker spectrometer at room temperature.

III. RESULTS and DISCUSSION

A. Structure of the composites

Fig. 2 shows the typical SEM images for FeNi/BMA-5 composites. The main picture gives distribution of FeNi MNPs over the subsurface layer of composite with 5 wt.% of MNPs. The inner structure of composite is uniform incorporating both aggregates, which are dominant, and small fraction of individual MNPs. Inset 1 gives the enlarged view of an aggregate. It consists of short chains of aggregated MNPs incorporated into asymmetrical three-dimensional loose globule. The size of globules varies from microns to several tens of microns. In the experimental section it was mentioned that the DLS characterization of mixed suspension used for the casting revealed de-aggregation of MNPs. The d_n was around 80 nm, i.e. far below the typical size of aggregates (Fig. 2. It means that re-aggregation of MNPs took place during the drying of the cast suspension. Most likely it happens due to the magnetic forces between MNPs. The volume fraction of FeNi MNPs in 5wt.% composite is only 0.6%. Therefore there is much free space between aggregates. If the filler content is increased the aggregates become closer to each other, overlap, and free space vanishes. Fig. 2(inset 2) shows image of a
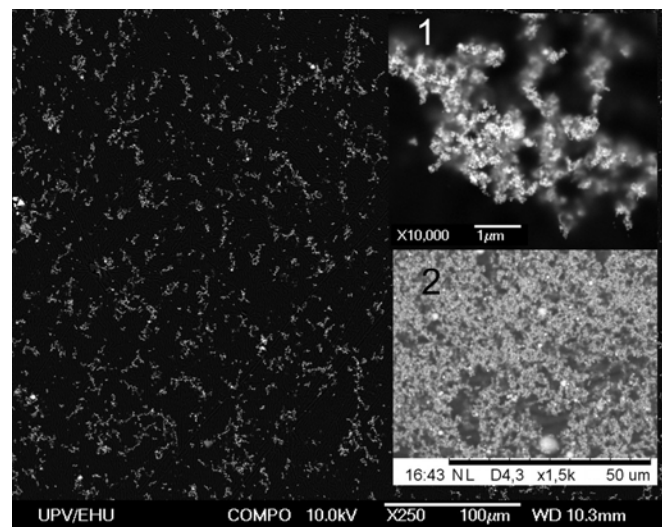

Fig. 2 SEM image of sub-surface layer of FeNi/BMA-5 composite with 5% MNPs content.

composite with 30wt.% of MNPs with "sponge-like" structure. It is mostly uniform and only few areas of relatively free space remain. Their size is 5 – 15 nm. The "sponge-like" structure contains below 4% of MNPs by volume, i.e. the structure remains loose. Most likely the value 4% might be taken as the estimation for the packing density of MNPs in an individual globule (Inset 1, Fig. 1). This value is very close to the typical

packing density in the coil conformations of the flexible macromolecular chains of organic polymers in their solution, which varies in the range 1 – 5% depended on the degree of polymerization [Rubinstein]. It makes us suppose that MNPs aggregates are topologically similar to the entangled polymeric macromolecules. The analogy between MNPs aggregates and polymeric chains is widely discussed in the literature[Iskhakova2002, Tavares 2006].

B. Interaction between MNPs and polymeric matrix

The enthalpy of interaction at the solid/polymer interface can not be measured in the direct calorimetric experiment as the solid particles do not spontaneously mix with polymer matrix. In such cases the enthalpy can be determined the appropriate Hess cycle of thermodynamics, which comprises the following steps for the process of the formation of polymeric composite [Safronov2012]: 1) Polymer + filler = Composite + ΔH_{comp}; 2) Polymer + solvent = solution + ΔH_1; 3) Filler + solvent = suspension + ΔH_2; 4) Solution + suspension = mixed suspension + ΔH_3; 5) Composite + suspension = mixed suspension + ΔH_4. As the polymer and the filler are mutually insoluble the only source for the enthalpy change upon the formation of composite is the interaction at their phase boundary. Therefore, ΔH_{comp} stands for the interaction between FeNi MNPs and polymer matrix. It was calculated according the equation: $\Delta H_{comp} = (1-\omega) \Delta H_1 + \omega \Delta H_2 + \Delta H_3 - \Delta H_4$, where ω is the weight fraction of MNPs in the composite. Fig. 3 gives the dependence of ΔH_{comp} in J/g of composite on the weight fraction of MNPs content in it. The values of ΔH_{comp} are negative over the entire composition range. It indicates that interaction between polymeric matrix and MNPs is energetically favorable. The largest absolute values of ΔH_{comp} (minimum on the curve) are obtained at 80 – 85 wt.% of MNPs in the composite. The only source for the enthalpy change is the interaction at the surface of MNPs. It results in the formation of the layer of polymer adsorbed on the surface. If polymer content is low (high ω) there is no enough polymer to provide saturated adsorption layers on the surface of MNPs and absolute ΔH_{comp} values are low. They increase with the diminishing of filler content and achieve maximum if polymer adsorption layers become saturated (minimum on the curve). Further decrease in MNPs content leads to the diminishing of ΔH_{comp} absolute values. It does not mean, however, that interaction is weakening. It is essential that ΔH_{comp} is related to 1 g of composite and so the fraction of adsorption layers goes down at low MNPs content (high polymer content). Therefore the enthalpy of formation of the saturated layer at high polymer content is divided by the growing denominator, which includes not only the amount of polymer in the adsorption layer but also the increasing amount of the bulk polymer. To extract the characteristic parameters of the interaction on the surface the curve in Fig. 3 was fitted by the model equation introduced for the enthalpy of interaction between polymer and solid filler in a composite [Safronov2012]:

$$\Delta H_{comp} = \Delta H_{ads}^{\infty} \frac{K(1-\omega)\omega S_{sp}}{K(1-\omega)+S_{sp}\omega} - \varepsilon_{coh}\varphi_p\gamma \exp\left(-\frac{(1-\omega)}{S_{sp}\omega\rho_p L}\right) \quad ,(3)$$

Here ΔH_{ads}^{∞} is the characteristic enthalpy of polymer adsorption at the solid surface per 1 m^2, K is the effective constant of adsorption, ε_{coh} is the cohesion enthalpy of polymer matrix per 1 g of polymer, φ_p is the volume fraction of polymer in composite, ρ_p is the density of polymer, L is the characteristic thickness of the adsorption layer, γ is the excess fraction of metastable voids in the glassy structure of polymer at the surface. For for BMA-5 ε_{coh} = 310 J/g was calculated based on atomic increments using quantum mechanics software package CAChe 7.5 [X]. MNPs content and volume fraction of polymer were calculated from the composite composition. ΔH_{ads}^{∞} , K, L, and γ were adjustable parameters. The result of the fitting is given as line in Fig. 3; it nicely matches the experimental points. The corresponding parameters were ΔH_{ads}^{∞} = -0.53 J/m^2, K = 100 m^2/g, L = 26 nm, γ =. 0.015. The first term in Equation (3) stands for molecular interaction between polymer and the solid surface, while the second term describes the
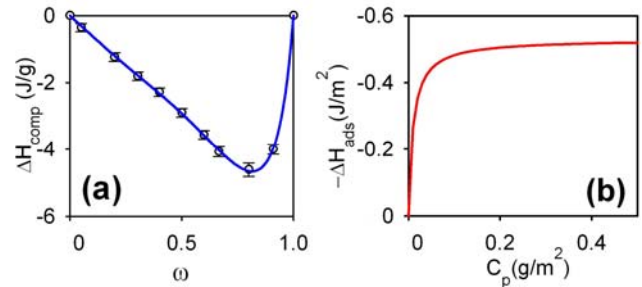

Fig. 3 (a) Dependence of the enthalpy of FeNi/BMA-5 composite formation on MNPs weight frac-tion. Enthalpy of formation is related to 1 g of composite. T=250C. Line corresponds to the fitting of experimental points by Equation (3). (b) Adsorption isotherm of BMA-5 polymer on the surface of MNPs in composite.

structural changes of polymer at the adsorption layer. The latter term is irrelevant in the framework of the present study and we will focus on the interaction term. Parameters ΔH_{ads}^{∞} , K accounted for the interaction of polymer and solid surface of MNPs in composite originate from the Langmuir-type equation (4), which proved to be appropriate for the filled polymer composites [Safronov2012]

$$\Delta H_{adh} = \Delta H_{adh}^{\infty} \frac{KC_P}{1+KC_P} \quad (4)$$

Here C_p is the effective concentration of polymer per 1 m^2 of MNPs surface given by the following equation: $C_P = \frac{1-\omega}{\omega S_{sp}}$.

Fig. 3b gives the adsorption isotherm of BMA-5 polymer on the surface of FeNi MNPs calculated using Equation (4) and ΔH_{ads}^{∞} , K values obtained in fitting procedure. One can see that due to the high value of the effective constant K the adsorption of BMA-5 steeply increases at polymer concentration below 0.1 g/m^2. Approximately 90% of the

adsorption is accomplished at 0.078 g/m^2. Using ρ_p=1.2 g/cm^3 one can estimate the thickness of the adsorption layer at this concentration. It gives ca. 60 nm, which is very close to the mean diameter of FeNi MNPs. The enthalpy of adsorption in saturated layer (-0.53 J/m^2) can be compared with the excess energy of metallic surface. Both experimental data [Tyson1977] and quantum mechanics calculation [Vitos1998] give 2.47±0.15 J/m^2 for the surface energy of Fe, and 2.33±0.16 J/m^2 for the surface energy of Ni. The reasonable estimation for the surface energy of FeNi would be around 2.40 J/m^2.

During the adsorption of polymer the surface energy diminishes due to the interaction between polymer and the surface. The summation of the surface energy and the enthalpy of adsorption might give the estimation of the surface energy of FeNi MNPs in composite. The resulting value of the surface energy is ca. 1.9 J/m^2. It is lower than that for pristine MNPs with metallic surface, i.e. polymer adsorption is favorable for the stability of composite. Meanwhile, the resulting value of the surface is still positive, and it means that the tendency for MNPs to aggregate preserves. It is likely the underlying reason for the formation of aggregates shown in Fig. 2.

Fig. 4(a) shows hysteresis loops of FeNi MNPs and 5 wt% of MNPs composite (Fig.4.a). The obtained value of the saturation magnetization M_s = 125 ± 5 emu/g for MNPs and 120 emu/g for MNPs in composite (recalculated taking into account the concentration) are quite high being only 25% below M_s value for bulk FeNi of this composition. Slightly lover M_s value for composite cannot be seriously discussed as a tendency of M_s lowering due to interaction with polymer layer on the MNPs surface keeping in mind that recalculation is done for most diluted composite with 5% of MNPs. Small experimental error in concentration of the order of 0.1wt% is comparable with the observed M_s variation for MNPs in composite. The coercive field H_c = 0.19 ± 0.01 kOe and 0.22 ± 0.01 kOe for MNPs and composite accordingly. Substantial coercivity and high M_s value confirm that the majority of permalloy nanoparticles are in multidomain states and explain their pronounced tendency to aggregation. Higher initial magnetic permeability for the MNPs comparing with composite can be also understood as indication of interparticle interactions.

The room temperature microwave signal was very complex due to high zero field absorption (Fig.4b) which is typical for material with high electrical conductivity [Kurlyandskaya 2014]. For spherical particles we should expect an FMR (H_{res}) located at 3.3 GHz for f = 9.5 but zero field and FMR signals overlap resulting in a huge width of the convoluting signal. If we anyway calculate corresponding values of H_{res} as the field for dP/dH=0 H_{res} values show tendency to linear decay with the increase of the MNPs concentration In the composite precisely what one can expect for the case of the increasing interactions in the composites with higher MNPs concentration. High microwave absorption makes these composites good candidates for applications.
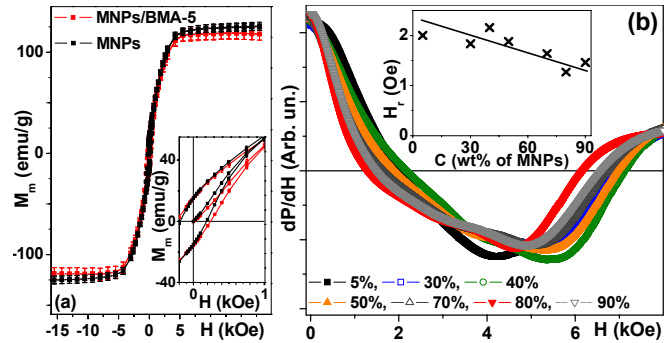

Fig.4. (a) Hysteresis loops of FeNi nanoparticles and MNPs in polymer matrix (5% concentration) Inset shows primary magnetization curves at better resolution. (b) Microwave absorption f = 9.5 GHz) for different composites.

IV. CONCLUSION

$Fe_{45}Ni_{55}$ MNPs with weighted average diameter of 69.5 nm were obtained by the EEW. FeNi MNPs/copolymer of 95 wt% butylacrylate and 5wt% methacrylic acid composites in the range of 5 to 90 wt% of MNPs were prepared and interaction between MNPs and polymeric matrix, the structure, magnetic and microwave properties of the MNPs and the composites were studied.

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