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Synthesis and Properties of Magnetically Operated Nanocomposites Based on Transition Metals Oxides

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Technique for synthesis magnetically operated nanocomposites based on transition metals oxides ($MeFe_2O_4$, Me = Fe^{2+}, Ni^{2+}, Co^{2+}) with biologically compatible coating $(SiO_2)_x$ were developed and optimized. Tetraethoxysilane (TEOS) and sodium silicate were used as precursors for formation of SiO_2 onto surface of magnetic component. Content of SiO_2 in nanocomposite surface layer were adjusted from 0.1 g to 1.0 g for 1.0 g of magnetic component.

Structure of the obtained nanocomposites was studied using XRD method, electron microscopy and IR-Fourier spectroscopy. Influence of adsorbents composition on their magnetic properties was studied using vibration magnetometer. It was shown that values of specific magnetization at saturation for nanocomposites containing 0.2 g of non-magnetic component per 1 g of magnetic component corresponds to the typical values of pure magnetic phase. With increasing of content of non-magnetic components a decrease of specific magnetization at saturation was revealed.

Keywords: surface modification, transition metals oxides, magnetically operated nanocomposites, Co ferrite, Ni ferrite, magnetic materials, biologically compatible coating.

INTRODUCTION

Complex metal oxides of the general formula $M^{II}M^{III}{}_2O_4$ with spinel structure have long attracted the attention of researchers and have extensive practical application from catalysts to magnetic materials [1, 2]. Compounds in which ion Fe_{III} acts as cation M_{III} called ferrites. In ferrites between the unpaired electrons of transition metal atoms strong exchange interaction takes place leading to ferrimagnetism with a Curie temperature well above room temperature [3]. Traditionally, these compounds were used as magnetic materials for the cores of transformers, computer memory elements, magnetic recording etc. Recently, however, due to the development of new synthesis techniques that allow obtaining ultrafine particles of controlled size and properties, it was reported about new applications of iron-containing compounds with spinel structure [4 – 10]. For example, there is a potential usage of superparamagnetic nanoparticles spinels in medicine for local hyperthermia and targeted delivery of drugs in the body, as well as in some catalytic processes [11 – 13].

Directional surface design and chemical engineering of nanocomposites layers opens enormous opportunities for creating unique magnetically adsorbents and next-generation drugs. Mesoporous materials formed by template synthesis have attracted increasing attention as potential materials for catalysis, separation and adsorption of molecules. Such materials have a developed specific surface (up to 1500 m^2/g) and small external surface. These characteristics determine high selectivity of catalysts and adsorbents based on them with negligible influence of processes occurring on the outer surface.

In this paper were present one of the possibilities of forming a surface layer of a nanocomposite magnetic component/SiO_2 using template synthesis. The main goal was to create a porous silica shell on the particles of Fe_3O_4, $NiFe_2O_4$, $CoFe_2O_4$ using sol-gel method [14], and eventually getting a mobile magnetically operated nanocomposite with well-developed surface layer.

EXPERIMENTAL DETAILS

In this paper, we have obtained complex ferrite particles on the basis of the magnetite, where the divalent iron ions were replaced by ions of metals (Ni, Co).

Magnetite was synthesized by the reaction of co-precipitation of salts of bi- and trivalent iron in aqueous ammonia solution according to the Elmore method [15, 16].

Obtaining the magnetic particles with an estimated low-point temperature of phase transition (Curie-Neel point) was performed by co-precipitation of metal salts in alkaline medium in the form of their oxides, followed by drying in a desiccator or in a special oven [17, 18].

The process of obtaining magnetite absolutely did not require additional energy, which means it runs at normal temperature (20 °C – 25 °C). Upon receipt of such a class of ferrites it is only necessary to observe the relationship between the bi- and trivalent iron. It should be Fe^{3+}/Fe^{2+} = = 2/1. A very important condition for the reaction is an excess of used precipitant (approximately tenfold by volume or concentration), and intensive stirring of the reaction mixture.

It was noted that the highest quality precipitate of ferrites can be obtained under the additional warming of the reaction mixture in a water bath at 80 °C – 90 °C for two hours and vigorously stirring. During the reaction of precipitation occurs the so-called "ripening" of precipitate,

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as noted its gradual transition of color from dark brown to black (like magnetite). As a result, we obtained the following ferrites: $NiFe_2O_4$ and $CoFe_2O_4$, which can be expressed by the equations of reactions:

$$MCl_2 \cdot 6H_2O + 2FeCl_3 \cdot 6H_2O + 8NaOH = \\ = MFe_2O_4 + 8NaCl + 20H_2O, \quad (1)$$

where M: Co^{+2}, Fe^{+2}.

The surface layer was formed by tetraethoxysilane (TEOS) and sodium silicate. To create a developed porous structure of the composite additives (solvents, surfactants, polymers) were used, which were removed during the process of thermal treatment and washing.

As template were selected block copolymer (poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol), $M_r = 8400$ amu) (P-123), sodium dodecyl sulfate and benzyl ammonium chloride, which were introduced into the process of alkaline hydrolysis of TEOS under continuous stirring.

Specific surface area of base ferrites, Fe_3O_4 and nanocomposites magnetic component/SiO_2 was measured using Sorptometer Kelvin-1042 (Coztech Instruments) by BET method using nitrogen gas as an adsorbate. A JEMOOCX-II transmission electron microscope was used to investigate the morphology of base ferrites and obtained nanocomposites.

X-ray diffraction analysis (XRD) was used to study structure of nanocomposites, identification of phase of magnetite, Ni, Co and calculation the average size of crystallites. The XRD analysis of the specimens was carried out on the DRON-4-07 diffractometer using filtered radiation of the cobalt anode lamp ($\lambda = 17.9021$ nm) with standard Bragg-Brentano focusing geometry.

To determine the presence of SiO_2 layer in nanocomposites measurements on Fourier Transform Infrared (FT-IR) spectrometer NEXUS (Thermo Nicolet) in the frequency range (600 – 4000) cm^{-1} were performed.

For studying magnetic properties of obtained nanocomposites vibrating magnetometer was used. The frequency and amplitude of vibration for samples were specified by the oscillator and the amplifier of low frequency. Measurements of demagnetized dry powders [19] were carried out at room temperature on frequency 228 Hz. Based on the experimental results cyclic dependencies of magnetization value (σ) versus applied magnetic field (H) – the hysteresis loop were built.

RESULTS AND DISCUSSION

Based on an analysis of obtained experimental results regularities of changes in the structure and properties of nanocomposites magnetic component/SiO_2, synthesized using above mention precursors were established. Some results are shown in Figs. 1 – 4.

With the increase of SiO_2 content in the surface layers of nanocomposites magnetic component/SiO_2 surface area predominantly increases. The maximum value of specific surface area ($S = 318$ m^2/g) is achieved for the amount of template introduced into the process of hydrolysis of TEOS of 0.0007 g.

Transmission electron microscopy has shown (Fig. 1) that the synthesized cobalt, nickel, and magnetite spinel are nanosized spherical particles of diameter 3 nm – 15 nm, which are joined into weakly coupled assemblies. Micro electron-diffraction pattern of the investigated powders has a characteristic annular structure with a pronounced diffuse peak at small angles (Fig. 1).

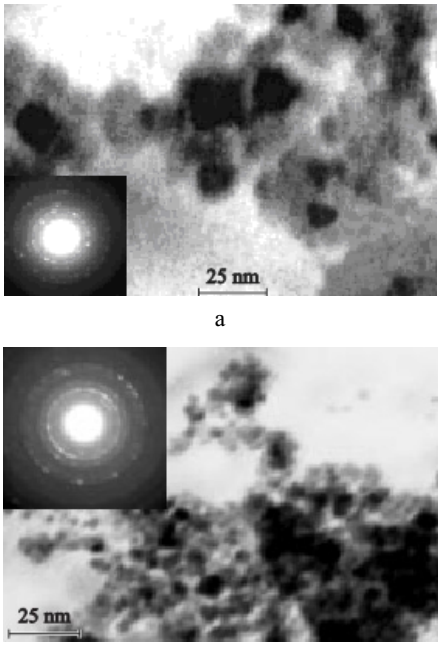

Fig. 1. TEM images of nanosized ferromagnetics oxides: magnetite (a) and cobalt ferrite (b)

Fig. 2 shows X-ray diffraction pattern of $CoFe_2O_4/SiO_2$ (a), $NiFe_2O_4/SiO_2$ (b) and Fe_3O_4/SiO_2 (c) nanocomposites. X-ray diffraction peaks for all samples are completely consistent with that taken from literature for corresponding ferrites [20]. Weak diffuse scattering at small angles indicates the presence in the samples a small amount of amorphous state along with the crystalline phase. Moreover on diffraction patterns for all samples weak peaks corresponding to hematite α-Fe_2O_3 were observed.

The presence of SiO_2 coating in nanocomposites shows decrease in intensity of reflections on corresponding diffraction patterns, for example in Fe_3O_4/SiO_2 (Fig. 2, c). With a minimum content of modifier on the diffraction pattern a weak peak at $2\theta = 38.5°$ is present, which corresponds to the most intensity reflection of the α-Fe_2O_3 crystal lattice (JCPDS №33-664). This suggests that such coverage is not enough to form a continuous layer of SiO_2 onto the magnetite surface and promote oxidation of the surface. However, further increase of SiO_2 content in nanocomposites results in disappearing of α-Fe_2O_3 phase due to the formation of a continuous layer of SiO_2 onto the magnetite surface. Based on these studies, as well as on data from [21, 22] it was estimated that the minimum thickness of the layer, which prevents oxidation of magnetite particles, ensured by modifying the 0.15 g – 0.18 g SiO_2 per 1 g of magnetite (1.5 mg – 1.8 mg per 1 m^2 of magnetite).

Presence of SiO_2 coating in nanocomposites was confirmed by the method of Fourier-transform infrared spectroscopy for all nanocomposites synthesized with different precursors. For example, for the Fe_3O_4/SiO_2 nanocomposite for the content of silicon oxide 0.68 g per 1 g

of magnetite (sodium silicate uses as precursor) observed absorption bands (AB) at 1070 cm^{-1} and 799 cm^{-1}, which corresponds to SiO_2 (Fig. 3) [23]. It is known from the literature that the absorption bands at 1070, 798, 460 cm^{-1} belong to the Si–O–Si bonds in silica, 970 cm^{-1} – stretching vibrations of Si–O in the Si–OX group (X – in most cases H or Me) [24]. In addition to these AB, there is also a diffuse absorption band in the frequency range (3000 – 3600) cm^{-1}, which corresponds to the vibrations of the hydroxyl groups of water in the liquid phase associated with the surface of oxides [24].

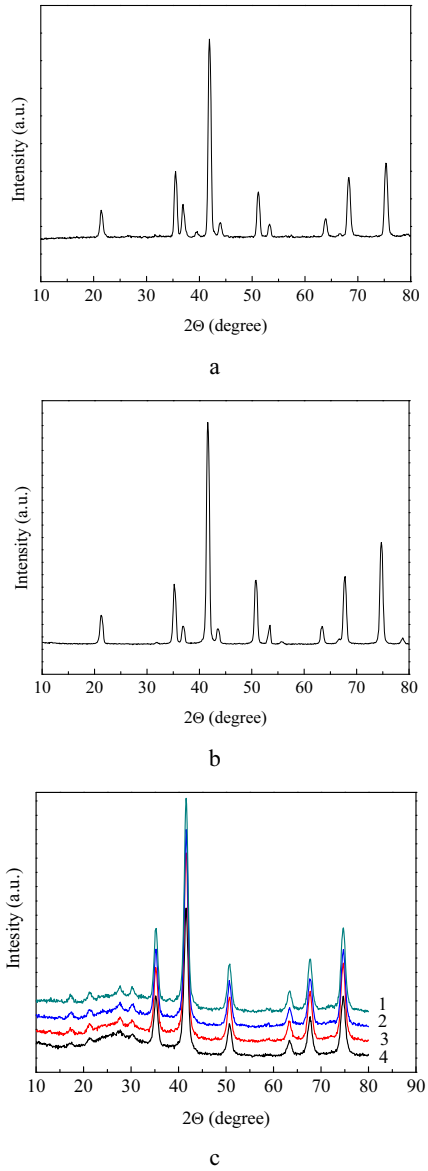

Fig. 2. X-ray diffraction patterns for nanocomposites $CoFe_2O_4/SiO_2$ (a), $NiFe_2O_4/SiO_2$ (b) and Fe_3O_4/SiO_2 (c), amount of surfactant: 1 – Fe_3O_4; 2 – 70 mg; 3 – 35 mg; 4 – 7 mg

Samples of nanocomposites Fe_3O_4/SiO_2, $NiFe_2O_4/SiO_2$, $CoFe_2O_4/SiO_2$ obtained using sodium silicate, as well as similar samples, where TEOS used as precursor, are characterized by a narrow hysteresis loop (Fig. 4), which is typical for nanocrystalline materials [23].

For the Fe_3O_4/SiO_2 nanocomposite samples containing 0.5 g of SiO_2 per 1 g of magnetite specific magnetization at saturation is $\sigma_s = 4.02$ μTl·m^3/kg and coercive force is $H_c = 6.26$ kA·m.

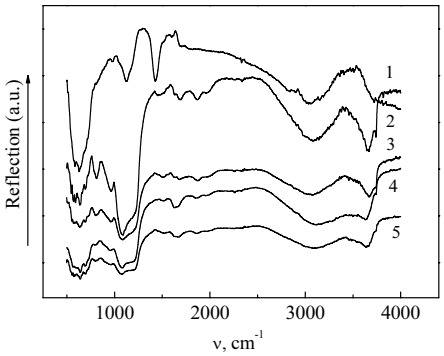

Fig. 3. IR-Fourier spectra of Fe_3O_4/SiO_2 nanocomposite, amount of surfactant: 1 – Fe_3O_4; 2 – 3.5 mg; 3 – 7 mg; 4 – 35 mg; 5 – 70 mg

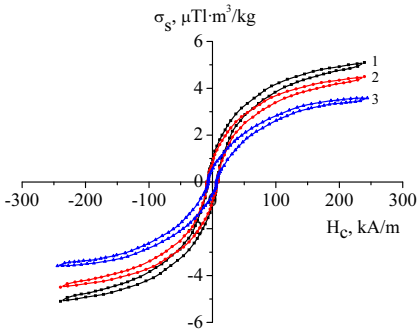

Fig. 4. Hysteresis loop for samples Fe_3O_4/SiO_2. Content of SiO_2 per 1 g of Fe_3O_4: 1 – 0.2 g; 2 – 0.5 g; 3 – 1 g.

Considering the magnetic properties of $NiFe_2O_4/SiO_2$ and $CoFe_2O_4/SiO_2$ nanocomposites it was found that all nanocomposites are characterized by narrow hysteresis loop. Furthermore, it was observed a decrease of specific magnetization at saturation when compared to non-modified ferrites and nonmonotonic variation of coercive force. Thus, with increasing SiO_2 content in the surface layer of the nanocomposite $NiFe_2O_4/SiO_2$ from 0 g to 0.2 g per 1 g of ferrite, σ_s decreased from 4.0 to 3.9 μTl·m^3/kg and H_c – from 7.56 kA/m to 5.9 kA/m; σ_r – from 0.23 to 0.15 μTl·m^3/kg. Further increasing of SiO_2 content to 0.8 g and 1 g per 1 g of ferrite leads to a reduction of σ_s from 3.18 to 2.86 μTl·m^3/kg and increase of H_c from 6.21 to 7.8 kA/m, respectively. For the $CoFe_2O_4/SiO_2$ nanocomposite containing 0.2 g of SiO_2 per 1 g of ferrite σ_s is 1.61 μTl·m^3/kg, H_c – 32.3 kA/m, σ_r – 0.26 μT·m^3/kg.

Thus, it can be argued that for high values of specific magnetization at saturation is necessary to choose the best mass of non-magnetic coverage for magnetic core of nanocomposite. One also needs to carefully carry out the synthesis of nanocomposites, to choose efficient synthesis conditions and to take into account the adsorption capacity of the surface layer.

CONCLUSIONS

Designed and optimized methods for synthesis of magnetically operated nanocomposites based on transition

metal oxides ($MeFe_2O_4$, $Me = Fe^{2+}$, Ni^{2+}, Co^{2+}) with a biocompatible coating $(SiO_2)_x$ using precursor TEOS, sodium silicate and templates P-123, sodium dodecyl sulfate and benzyl ammonium chloride.

The relationship between structure, composition and magnetic properties of nanocomposites is established. It was shown that values of specific magnetization at saturation for nanocomposites samples magnetic component/SiO_2 containing 0.2 g of non-magnetic components per 1 g of magnetic component are close to the corresponding values of the initial components of the magnetic phase. A decrease of specific magnetization at saturation for the samples and the nonlinear change of the coercive force with increasing of content of non-magnetic components are revealed.

The obtained nanocomposites further will be used as adsorbents in medicine and biology.

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