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Magnetic Properties of the Cobalt Ferrous Spinel Ferrite Nanoparticles Formed on the Steel Surface Contacting with Cobalt Chloride Water Solutions in Open-air System

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The paper describes creation of cobalt ferrous spinel ferrite nanoparticles and investigation of their phase composition, surface structure and magnetic properties. Cobalt ferrous spinel ferrite nanoparticles were synthesized in an aerated system of steel electrode contacting with aqueous cobalt chloride at different pH values of solution. According to X-Ray diffraction data, it was shown, that some impurity phases also formed during the synthesis process, notably, lepidocrocite and goethite on the steel surface and Green Rust I, cobalt hydroxide, heterohenite in the solution. The quantity of such phases depends on pH value of initial solution. The size of synthesized cobalt ferrous spinel ferrite nanoparticles was approximately 10 – 12 nm. Saturation magnetization of synthesized cobalt ferrous spinel ferrite nanoparticles is rather high. Synthesized magnetic cobalt ferrous spinel ferrite nanoparticles are promising for different medical-biological applications.

Keywords: nanoparticles, cobalt ferrous spinel ferrite, magnetic properties.

PACS numbers: 75.50. – y, 75.75. – a, 78.67.Bf, 81.07. – b

1. INTRODUCTION

Among the ferrimagnetic nanoparticles that are usually used for medical-biological purposes magnetite and ferrites, especially cobalt ferrous spinel ferrite, are the most applicable [1]. Due to their physicochemical properties such particles are perspective materials for creating magnetic carriers for a target drug delivery, a catalyst of oxidation processes in living organisms and sorbents for separation of biological objects [2]. According to literature sources, the main methods of nanosized ferrimagnetics synthesis are their obtaining in oxygen-free low-alkaline water solution containing cobalt, ferric or ferrous salts, sol-gel synthesis, the reverse micelles method, the high-temperature synthesis and others [3]. At the same time, spinel ferrite nanoparticles are formed by electrochemical process on the steel surface when the latter contacts with air oxygen and water solution [4]. The following parameters of ferrite nanoparticles synthesis such as dispersion medium chemical composition, temperature and oxidizing conditions influence the phase composition, morphology and nanoparticle size, as well as their aggregative stability. The difference in the methods of the nanoparticles obtaining can change their properties, for example, magnetic ones [5].

The purpose of the present work is to investigate the magnetic properties of the cobalt ferrous spinel ferrites nanoparticles formed on the steel surface by contact with cobalt chloride water solution in the open-air condition.

2. MATERIALS AND METHODS

2.1 Materials

Formation of the iron oxide particles was carried out in an aerated system of steel electrode contacting with aqueous dispersion medium. The disk electrode was made from finished steel (St3), consisted of, %: C – 0,14-0,22; Si – 0,05-0,15; Mn – 0,4-0,65; Cr – 0,3; Ni – 0,3; P – 0,04; S – 0,05; N – 0,01. Before every experiment the steel surface was cleaned from oxidized layer with aqueous solution of sulfuric acid. As dispersion medium the $CoCl_2$ water solutions at $C_{Co(II)} = 100$ mg/dm^3 were chosen; the pH values were set from 2.5 to 12.0. The duration of the phase formation process has been 48 h when the system passed to the stationary state.

2.2 Methods

As the main methods of the investigation the X-ray diffraction (XRD), X-ray fluorescence analysis, Scanning Electron Microscopy (SEM) and chemical analysis were used. Magnetic properties of nanoparticles were studied by magnetometry method.

3. RESULTS AND DISCUSSION

Analysis of XRD data allow to identify the phase composition and particle size of the surface structures depending on the pH values of their obtaining. So, at pH = 2.5 the spinel ferrite reflexes ((111), (220), (311), (400), (422), (333, 511), (440), (533)) as well as γ-FeOOH reflexes (020), (120), (031), (051, 200) are present on the XRD-pattern. As additional structure goethite α-FeOOH ((110), (130), (121), (211), (250)) appears simultaneously, but it reflexes are weak. The size of the $(Co_x, Fe_{(1-x)})Fe_2O_4$ nanoparticles obtained in such condition is ~ 14 nm. The Fe : Co ratio of the surface atoms on the $(Co_x, Fe_{(1-x)})Fe_2O_4$ is 95.8 : 4.2. At the pH value of the cobalt chloride solution 4.0, the quantity of the spinel ferrite phase grows and quantity of the iron oxyhydroxides (lepido-

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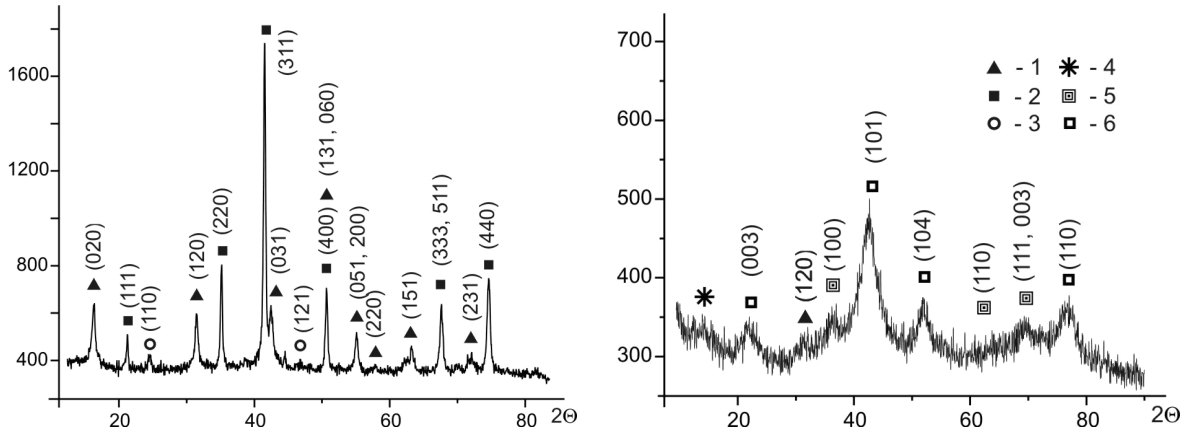
crocite and goethite), on the contrary, decreases. The particle size of $(Co_x, Fe_{(1-x)})Fe_2O_4$ is smaller than at pH = 2.5, namely ~ 10.5 nm. The ratio of Fe : Co on the spinel ferrite surface is 92.0 : 8.0. At pH = 6.5 the main surface structure is cobalt ferrous spinel ferrite. Its average particle size is ~ 10.8 and Fe : Co atom ratio is 93.8 : 6.2. At pH = 9.5 on the steel surface spinel ferrite and lepidocrocite are formed. Under such conditions the spinel ferrite particle size reaches ~ 12 nm and Fe : Co ratio is 100 : 0, so, reflexes at XRD pattern belong to magnetite $FeFe_2O_4$. The phase composition of the precipitates from the solutions formed in the pH range from 9.5 to 12.0 includes Green Rust I, amakinite $Fe(OH)_2$, lepidocrocite γ-FeOOH, cobalt hydroxide $Co(OH)_2$ and heterohenite CoO(OH). The spinel ferrite phase is absent under such condition. The surface Fe : Co atom ratios for the phases obtained in the dispersion medium are: at pH = 9.5 – Fe 42.4 : Co 57.6; at pH 11.0 – Fe 19.0 : Co 81.0, and at pH = 12.0 – Fe 9.7 : Co 90.3, respectively.

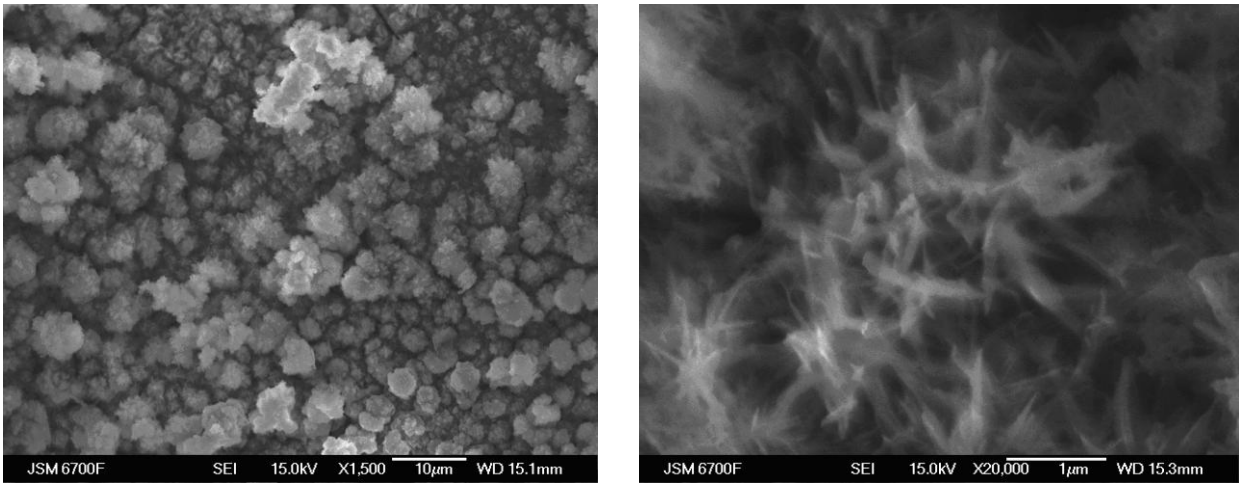
Fig. 1 shows the XRD patterns of the structures formed on the steel surface contacting with $CoCl_2$ water solution at the pH = 9.5 (a) and weak crystallized phases formed in the solution (b).

Fig. 2 shows the SEM-images of cobalt ferrous spinel ferrite (a) and lepidocrocite (b).



a b

Fig. 1 – The diffraction patterns of the nanosized structures formed by contact of the steel electrode with $CoCl_2$ water solution at the pH = 9.5: a – on the steel surface; b – in the solution. The numbers correspond to the phases: 1 – lepidocrocite γ-FeOOH; 2 – spinel ferrite; 3 – goethite α-FeOOH; 4 – Green Rust I, 5 – cobalt hydroxide $Co(OH)_2$; 6 – heterohenite CoO(OH)



a b

Fig. 2 – SEM image of the structure formed by contact of steel with water solution containing cobalt 100 mg/dm³: a – cobalt ferrous spinel ferrite; b – lepidocrocite

Fig. 3 shows hysteresis loops of two samples: sample, synthesized by pH = 4.5 (a) and sample, synthesized by pH = 6.5 (b), both on the steel surface. It was shown, that saturation magnetization for the sample, synthesized at pH = 4.5 was M_s = 32 A·m²/kg, its remanence magnetization was M_r = 15 A·m²/kg and coercitivity H_c = 0,05 T. Saturation magnetization for the sample, synthesized at pH = 6.5 was M_s = 40 A·m²/kg, its remanence magnetization was M_r = 18 A·m²/kg and coercitivity H_c = 0,05 T.

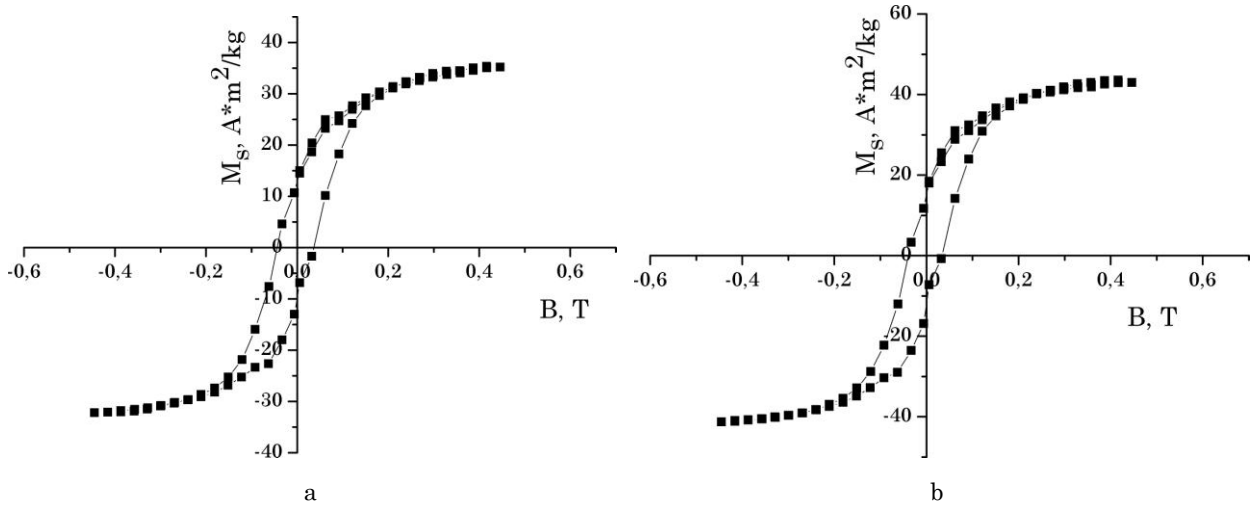


Fig. 3 – Hysteresis loops of samples, synthesized on the steel surface by pH = 4.5 (a) and pH = 6.5 (b)

Saturation magnetization of the sample on the steel surface, synthesized at pH = 9.5 was $M_s = 14$ A·m^2/kg, but this sample doesn't show remanence magnetization and coercitivity. Saturation magnetization of sample, synthesized at pH = 12.0 was very weak. Samples, obtained from the solution don't show saturation magnetization.

So, one could conclude, that samples, synthesized on the steel surface at pH values of 4.5 and 6.5 have rather high saturation magnetization, so they could be used in many medical-biological applications.

4. CONCLUSIONS

1. The phase composition of the iron-oxygen nanosized structures that are formed on the steel surface contacting with cobalt chloride water solution in the open-air system depends on the physicochemical conditions of the experiment. One of the parameters including the process of the phase formation is the pH values of the dispersion medium contacting with steel surface. According to XRD data cobalt ferrous spinel ferrite phases play the important role among the surface structures formed on the steel surface in the wide range of pH values (from 2.5 to 9.5). Depending on the experimental condition the particle size and Fe : Co surface atom ratios are changed that lead to the difference in magnetic properties of the samples.

2. Synthesized magnetic cobalt ferrous spinel ferrite nanoparticles are promising for different medical-biological applications.

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