

Synthesis of Cobalt Ferrite Nanoparticles by Ultrasonic Wave-Assisted Technology

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Abstract - Powders of finely dispersed cobalt ferrite were obtained by sonication. With the help of X-ray analysis, scanning electron microscopy, the influence of the initial pH of the solution and the processing conditions on the properties of the compounds formed was investigated. Samples were obtained from precursors having different pH values ranging from 7.0 to 12.0. It has been established that at pH 7-10, cobalt ferrite is formed by the mechanism of incorporation of cobalt cations into the crystal lattice of magnetite. At pH = 10 is magnetite. Single-phase cobalt ferrite is formed at pH = 12. The dependence of the coercive force and the saturation magnetization on the initial pH is established. The maximum values of the coercive force 460.3 Oe and the saturation magnetization 61.3 emu / g correspond to a pH of 12. An increase in the particle size during sonication has been established. The size of the agglomerates is 1-10 μ m according to the electron microscopy data. The particle sizes calculated using the Scherrer formula were 35-70 nm.

Keywords: Cobalt ferrite Nano-particles Co-precipitation Composition Magnetic properties

I. INTRODUCTION

The interest of researchers to develop new and improve existing technologies for obtaining cobalt ferrite has been preserved for many years [1-20]. This is due to the emergence of new areas of its use. Among the numerous methods used in practice, good results have been obtained with the use of hydro phase technologies. The possibilities of using such technologies to regulate various structural, magnetic, technological properties are enormous. In this case, it becomes possible to obtain fine particles having a set of specific properties.

The authors of [12,13,15-17] used the co-precipitation method in the synthesis of cobalt ferrite. Recently, this method has been modified in such a way as to synthesize nanosized compounds using additional hydrothermal, ultrasonic or thermal treatment. In some cases, citrates, tartrates or oxalates are used as promising precursors. The authors of [11-13,18,19] used high-temperature treatment of the previously obtained sol.

The use of sonochemical synthesis has great advantages in the case of the need for the preparation of dispersed powders. At the present time, the enormous experimental material available is of a contradictory nature due to the complexity of the systems under study. The technology under consideration attracts with simplicity of hardware design and the ability to regulate the composition of the formed compounds. The use of ultrasound has many advantages (low-cost precursors, quick response, energy saving, simplicity of hardware design).

The purpose of this study is to determine the possibility of obtaining cobalt ferrite using ultrasound and to assess the possibility of regulating the properties of the product obtained. In the course of preliminary studies, it was found that it is the technological parameters that significantly influence the course of the reaction and the composition of the products obtained.

II. EXPERIMENTAL

Production of co-precipitated compounds was carried out by pouring under continuous stirring the appropriate mixture of sulphate solutions with the required ratio of cations as in the ferrite. We used 0.5 M solutions of iron and cobalt salts analytical grade.

Polyhydrocomplex sol obtained at different pH was treated with ultrasound in a laboratory setup. pH range 7-12, period - 1. It consisted of a ceramic reaction vessel, in which the ultrasonic dispersant transducer USDN-2R was immersed and connected to the generator of ultrasonic vibrations. We investigated the influence of ultrasound at a frequency of 22 kHz and the ultrasonic intensity at the load within 1 MW/m².

The study of the phase composition of the samples was carried out using X-ray diffractometer DRON - 2.0 in Cu-KD-monochromatic radiation. Scanning was performed at room temperature in the angles range of 5-85°, period=0,04 s.

The pH of the solution has been monitored at regular intervals by means of pH meter-pH-150 MI. pH ranges 7-12, period - 1. The XRD studies were carried out using a DRON-2.0

The value of the lattice constant parameter a_{th} , for $\text{q}\text{iFe}_2\text{O}_4$ was determined from the position of the principal peak, using the relation

$$d = \frac{a_{th}}{\sqrt{h^2 + k^2 + l^2}},$$

where d is the interplanar spacing and h , k and l are the Miller indices; the obtained values of the lattice constant. For all samples, the Scherrer formula:

$$D \sim 0.89 \lambda / \Delta 2\theta$$

$$E \sim \cos T$$

where λ is the X-ray wave length; θ is the Bragg diffraction angle and $\Delta 2\theta$ is the full width at half maximum (FWHM), was used to calculate the average size D of the crystallites.

The microstructure of the nanoparticles obtained was investigated by scanning microscopy with a help of Remme-102 microscope. The study of the magnetic properties of cobalt ferrite nanopowders was performed by vibrating magnetometry.

III.RESULTS AND DISCUSSION

Ultrasonic treatment is often used to intensify oxidation processes in various technologies. These processes are based on the generation of free radicals and active oxidants. Possible mechanisms, including the most probable processes that occur in a cavitation bubble, have been described by many investigators [20-22]. The basic idea of carrying out ultrasonic treatment is based on the effect of cavitation, which consists in the fact that when a powerful acoustic wave passes through a liquid, cavitation bubbles arise in which pressure, temperature, electric discharges and explosions increase strongly, which leads to the appearance of various physical-chemical processes that are not observed under other conditions. According to calculations, up to 100 MPa and 10000 K respectively. The release of a significant amount of energy during the closure of cavitation bubbles leads to the sonolysis of water with the formation of a number of radicals (HO \cdot , NO $_2\cdot$, etc.), oxidants (O $_3$, H $_2$ O $_2$), which participate in the oxidation-reduction reactions [21]. The high activity of the formed products of sonolysis makes it possible to obtain compounds with different properties. It is known that the phase composition of products formed during ultrasonic processing of products is diverse. The variable valence of the starting materials used in the synthesis and the oxidizing environment give grounds for assuming the possibility of formation of undesired phases of mixed oxyhydroxides, solid solutions of hematite, lepidocrocite, goethite, hydrated oxides, etc.

To assess the effect of ultrasound, it is necessary to establish the composition and properties of products formed during ultrasound treatment. According to experimental data, with increasing pH in the system, the time of the oxidation process remains constant in the range of 7-11, and then increases jumpwise (Tab.1).

TABLE I DEPENDENCE OF THE OXIDATION TIME ON THE INITIAL PH OF THE SOLUTION

pH	W,min	pH	W,min
7	2,0	10	3,4
8	4,0	11	3,5
9	3,2	12	28,1

The increase in the oxidation time with increasing pH is explained by a decrease in the reactivity of the oxidizing agents. It is precisely these conditions of slow crystallization in supersaturated solutions that make it possible to obtain a crystalline product under hydro phase synthesis conditions. X-ray diffraction patterns are shown in Fig. 1.

The X-ray patterns contain reflections corresponding to the crystal lattice of the spinel of cubic syngony, which corresponds to JCPUS-22-1086 and also J-(CoFe) $_2$ O $_3$, (CoFe) $_3$ O $_4$.

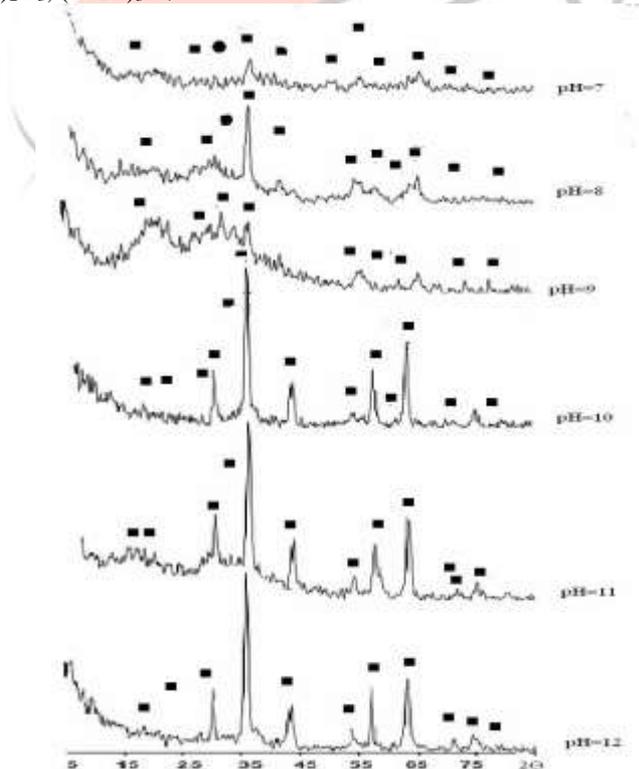


Figure 1. X-ray diffraction patterns of samples obtained at different pH, γ CoFe $_2$ O $_3$, - Co $_3$ O $_4$

At low pH values, an amorphous phase, the presence of which is due not complete the crystallization process. With increasing pH, the degree of crystallinity increases. However, the anomalously low values of the coercive force at pH 9-10 can be explained by the formation of the crystalline structure of maghemite with built-in cobalt cations. At pH 12, cobalt ferrite is formed, which is confirmed by magnetic measurements. A similar structure and similar reflexes make it difficult to qualitatively identify with the help of an x-ray phase analysis.

Figures 2 and 3 show measurements of the magnetization of samples obtained at different pH values. As follows from the figure, for all samples a magnetization of saturation and a hysteresis loop are characteristic in a magnetic field.

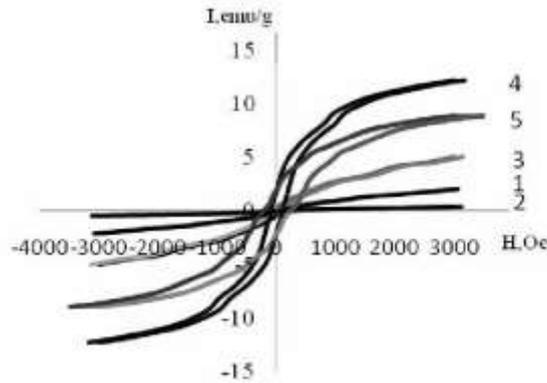


Figure 2. Magnetization curves at room temperature of the samples prepared at pH 1-7, 2-8, 3-9, 4-10, 5-11 T=293 K

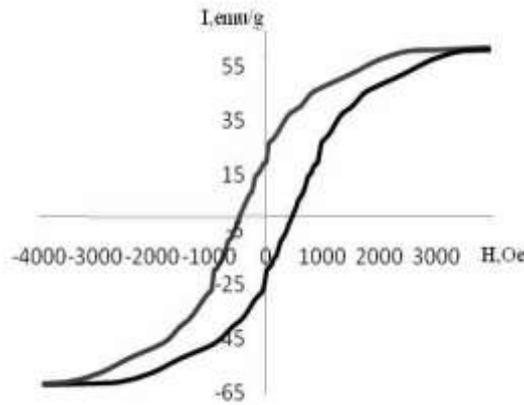


Figure 3. Magnetization curves at room temperature of the samples prepared at pH=12 T=293 K

The saturation magnetization of the samples varies from 0.5 to 61.3 emu/g. The coercive force was 50-450 Oe, respectively. This is much higher than the values given in [10]. It is known that fine-dispersed ferrimagnets possess special magnetic properties. The magnitude of the coercive force increases with the increase in the size of the crystallites. The dependence of the coercive force on the particle size is extreme, we can assume that the causes of the increase in H_c are the anisotropy of the particle shape, the magnetic anisotropy, and the size of the agglomerates corresponding to d_{cr} .

A comparative analysis of the nature of the magnetic saturation curves of I_{sat} and coercive force showed a correlation between graphs 4 and 5. This is primarily due to the fact that the magnetic characteristics depend to a greater extent on the composition of the compounds formed. The sequence of phase formation can be represented as follows: $J-(CoFe)_2O_3, o(CoFe)_3O_4 o CoFe_2O_4$.

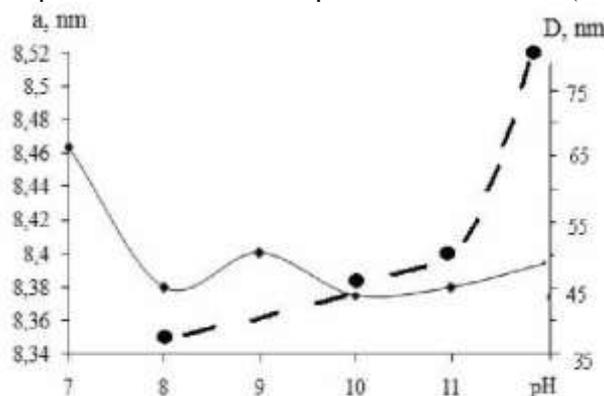


Figure 4. Dependence of the crystal lattice parameter (-), and size of crystallites (- -) on pH

The dependence of the size of the crystallites of the obtained powders on the pH is shown in Fig. 4. However, in the study of powders by means of electron microscopy, agglomerates were discovered that are substantially larger than size of the crystallites,

determined from the X-ray diffraction patterns.

Figure 5. Dependence of the coercive force and the magnetization of saturation on pH

The result obtained indicates that some of the particles synthesized by ultrasound form agglomerates. Thus, the calculated size of crystallites does not match the size of the Nanoparticles entering the agglomerates. Agglomeration of particles can be associated with the impact of ultrasound and the presence of magnetic interaction between them. Analysis of the curve of the dependence of the dimensions size of the crystallites on pH showed that in more solutions that are alkaline the average diameter of the Nanoparticles increases. Moreover, the average size of agglomerates is also increased. Figure 6 presents a typical photomicrograph of a cobalt ferrite sample obtained at pH = 12.

The powder is both individual particles and faceted composites of agglomerated particles of irregular shape of various sizes. Granulometric analysis of powders showed a large scatter of particles in size. The size of the agglomerates varies from 1 to 10 μm . Anisotropy of the shape of the particles is observed.

The data obtained show that the size of CoFe_2O_4 Nanoparticles is largely determined by the initial pH. As the pH of the synthesis increases, larger CoFe_2O_4 particles are formed.

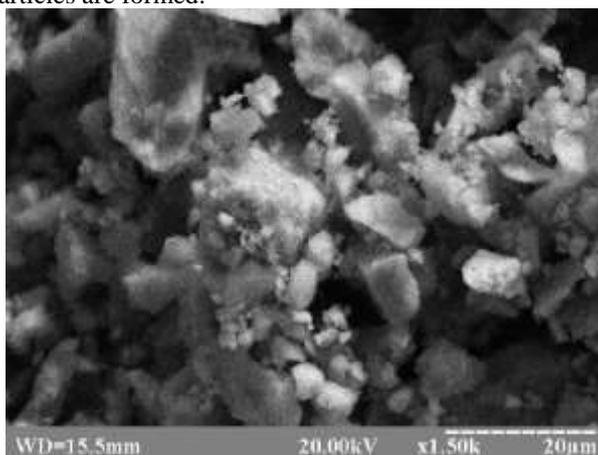


Figure 6. SEM images of CoFe_2O_4 powder

IV. CONCLUSION

Although a conclusion may review the main points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions. Authors are strongly encouraged not to call out multiple figures or tables in the conclusion these should be referenced in the body of the paper.

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