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FEATURES OF THE STRUCTURE OF MAGNETIC NANOPOWDERS OF IRON OXIDES IN VARIOUS METHODS OF THEIR SYNTHESIS

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Abstract

The article presents the results of obtaining iron oxide nanoparticles with magnetic properties – maghemite and magnetite, precipitated from solutions of ferrous and trivalent iron salts using various technological techniques. Depending on the deposition conditions, magnetic nanopowders corresponding to the composition of solid solutions of magnetite-maghemite were obtained. By methods of scanning electron microscopy and X-ray phase analysis, calculation of the parameters of the elementary cells of the crystal lattices of magnetite and maghemite, it is shown that the synthesis conditions affect the size and shape of nanoparticles and the degree of their aggregation. It was found that monophasic magnetite and maghemite do not form during chemical deposition, a solid solution of mixed composition precipitates.

Keywords: *iron oxides, maghemite, magnetite, chemical precipitation, nanoparticles, solid solution*

Magnetic nanoparticles of iron oxides (magnetite and maghemite) are increasingly being used in various branches of science and technology and especially in biomedical applications (Kurlandskaya, et.al, 2021; Marnautov, et.al, 2017; Wu, et.al, 2015; Corot, et.al, 2006). This is due to the unique magnetic properties of these materials, which largely depend on the phase composition, structure and morphology (size and shape) of the particles (Katz, 2019). These characteristics are significantly influenced by the conditions for obtaining nanoparticles (Chernova, et.al, 2022). To date, many methods for the synthesis of magnetic iron oxide nanoparticles are known, which are reflected in a number of scientific publications, including recent reviews (Tahir, et.al, 2021; Abilkosimova, et.al, 2024). The most technologically simple method is the joint precipitation of ferrous and trivalent iron salts from aqueous solutions (Taketomi, 1993). However, despite the apparent simplicity, the synthesis conditions by this method have a significant effect on the phase composition and morphology of particles, which ultimately affects their target properties. In

this regard, the interest in studying the factors determining the conditions for the synthesis of magnetic nanoparticles based on iron oxides is only increasing. It is known that magnetite, which has pronounced ferromagnetic properties, under oxidation passes into maghemite γ-Fe_2O_3, when heated to 230 ˚C, hematite is formed, as well as iron (III) oxide, but does not have magnetic properties (Nikiforov, et.al 2014). Since maghemite and magnetite are isostructural, the determination of the phase composition of nanoparticles is associated with the need to calculate the parameters of the crystal lattice, as well as with the involvement of a number of other physico-chemical research methods (Anthony, et.al 2018).

The aim of this work is to synthesize magnetic nanopowders of iron oxides by co-precipitation of trivalent and divalent iron salts from aqueous solutions by various methods and compare their structure and phase composition using modern analytical methods

Experimental

The salts $FeSO_4 \times 7H_2O$ and $FeCl_3 \times 6H_2O$ (pure for analysis, Sigma-Aldrich) and a 25% aqueous solution of ammonia were used in the work.

The deposition of magnetite was carried out by reaction

$$2FeCl_3 + FeSO_4 + 8NH_4OH = Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 4H_2O$$

To do this, 0.278 g. $FeSO_4 \times 7H_2O$ (1mmol) and 0.540 g. $FeCl_3 \times 6H_2O$ (2 mmol) were dissolved in 50 ml of bidistilled water at room temperature. 10 ml of 10% ammonia solution was injected into the resulting solution using a syringe. In the first variant, for the oxidation of magnetite into maghemite, precipitation was carried out under the influence of ultrasound (DSA50-SK1–1.8L. 50 W, 40 kHz) during the entire deposition process (30 min).

In the second variant, aqueous solutions of iron salts $FeSO_4$ and $FeCl_3$ were mixed, as in the first case, in the molar ratio $FeSO_4$: $FeCl_3$ = 1: 2, magnetite was precipitated with an aqueous solution of ammonia at an elevated temperature of 60 ˚C and bubbled with argon to remove dissolved oxygen and prevent oxidation and transition of magnetite to maghemite.

In the third variant, magnetite was obtained similarly to the previous variants, but neither ultrasound nor bubbling with an inert gas were used and the precipitate was kept for a day for complete maturation and partial oxidation of nanoparticles. The resulting precipitates were separated from the solution using a neodymium magnet, washed with distilled water and dried at 105 ˚C in a drying cabinet. Research methods. The phase composition and crystal structure of the powders were studied by powder radiography using the XRD-7000 MAXima diffractometer (Shimadzu). The lattice parameters were calculated using PDW in software. The particle size and degree of aggregation were evaluated using scanning electron microscopy (SEM).

As can be seen from (Fig. 1), in all three variants of synthesis (methods 1–3), nanoparticles are formed, the size of which does not exceed 20–30 nm. The resulting nanoparticles are prone to aggregation, which can be explained by residual magnetization. It can also be noted that the formation of spherical particles is observed under ultrasonic influence.

Figure 1. *SEM images of magnetic nanopowders obtained by chemical deposition using various techniques: method 1 – ultrasound, room temperature; method 2 – bubbling with inert gas, 60 °C; method 3 – room temperature, maturation during the day*

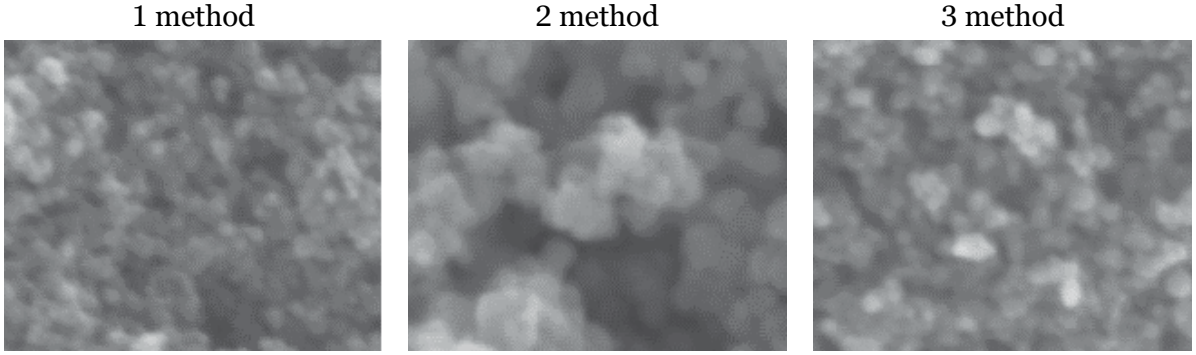
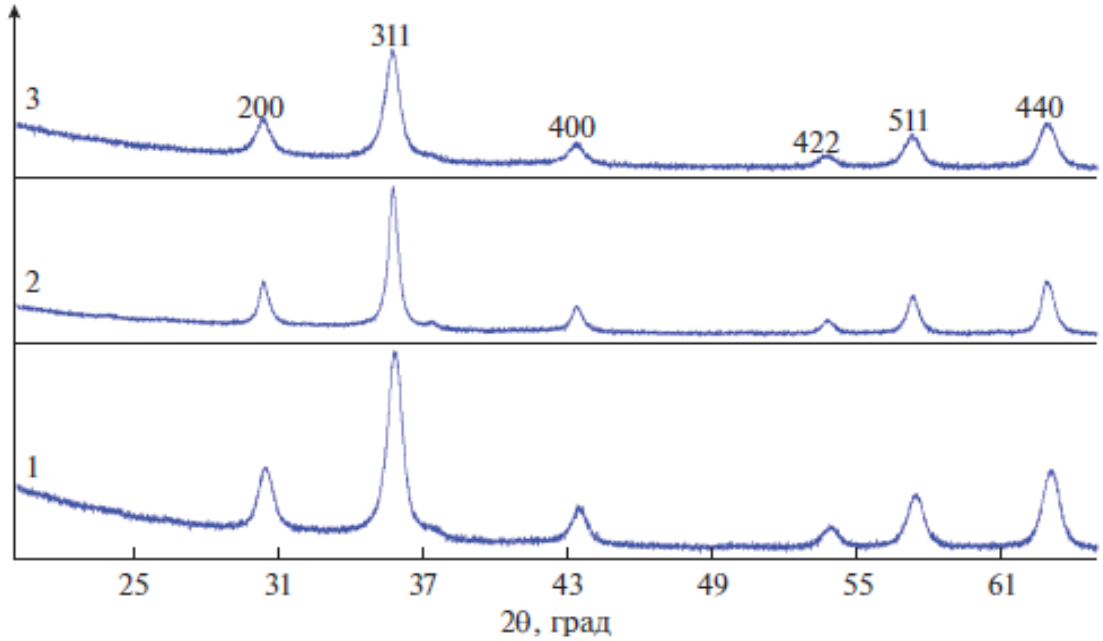


Figure 2. Shows X-ray images of the obtained iron oxide nanopowders

Figre 2. *X-ray images of magnetic nanopowders of iron oxides obtained by methods 1, 2and 3*



It follows from Figure 2 that all sediments correspond to the composition of magnetite-maghemite without significant impurities of any other phase. It is known that maghemite and magnetite have a common crystal lattice structure, which means that the positions of the diffraction peaks on their radiographs practically coincide. Therefore, based only on the analysis of the position of the peaks on the diffractograms of nanopowders, it is quite difficult to distinguish magnetite from maghemite. They can be distinguished by comparing the parameters of the unit cell.

Table 1 shows calculations of the parameters of the elementary cells of synthesized iron oxides, made on the basis of experimental and literary data.

Table 1. *Parameters of the elementary cells of the obtained nanopowders*

Title	*a*, A
Maghemite (Katz.2019)	8.336–8.339
Magnetite (Nasrazadani,1993)	8.396–8.397
Nanopowder synthesized	
by method 1	8.337
by method 2	8.350
by method 3	8.382

The results of the experiment and the calculations performed show that the nanopowder synthesized by method 1 under ultrasonic exposure, which possibly contributes to the oxidation of Fe(II) to Fe(III), is the closest in phase composition to maghemite (γ-Fe_2O_3). Elevated temperature and argon bubbling (method 2) contribute to the formation of trivalent iron oxide, while argon bubbling slowed down this process. The powder synthesized by method 3 is closer in size of the unit cell parameter to magnetite than the above samples. Obviously, exposure to mother liquor during the day has less effect on the oxidation of iron to a trivalent state.

The obtained results and conclusions are in good agreement with the results of the study by other authors (Shilova, et.al, 2020).

Conclusion

Nanopowders with a nanoparticle size in the range of ~10–25 nm were synthesized by chemical precipitation from aqueous solutions of iron (II, III) salts, corresponding to the compositions of magnetite-maghemite solid solutions, while the proximity of the resulting composition to the extreme members of a number of solid solutions depends on the synthesis conditions (ultrasound, bubbling, heating, duration of exposure in mother li-

quor). It is shown that the use of heating, bubbling with an inert gas, and especially ultrasonic exposure during the deposition of powders with an aqueous solution of ammonia promotes the formation of spherical nanoparticles and intensifies the oxidation of Fe(II) to Fe(III) and the formation of a solid solution, which is closer in composition to maghemite. It is noted that a longer maturation of the precipitate in the mother liquor increases the tendency of nanoparticles to aggregate, leading to the formation of nanoparticles that correspond to the composition of the solid solution, closer to magnetite.

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