Synthesis of nanostructured FePt systems

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Abstract. The paper compares some characteristics of nanoparticles of the FePt system obtained by the method of joint reduction of solutions of metal precursors using different reducing agents: an alkaline solution of hydrazine hydrate and sodium tetrahydroborate. The method of transmission electron microscopy is used to analyze the shape and morphology of the obtained nanosized particles, according to the data obtained by the methods of X-ray diffraction, phase analysis is carried out and the main X-ray structural parameters are evaluated. Thermal analysis in combination with mass spectrometry is used to characterize the state and purity of the surface of nanoparticles. It is shown in the work that nanoscale FePt systems obtained using the reductants selected in the work have similar physicochemical characteristics.

1. Introduction
In the last two decades, there has been a demand for an increase in the amount of stored information on solid-state media, while their miniaturization is required [1-5]. To achieve these requirements, nanoscale materials with high magnetic characteristics are required, such as FeCo and FeNi FePt nanoparticles [6-10].

It is known [11-14] that the size, morphology and other practically relevant characteristics are determined by the method of obtaining nanosized particles. One of the most widespread methods for the synthesis of FePt nanoparticles, which are distinguished by their instrumental simplicity, is the joint reduction of aqueous solutions of metal precursors [15]: H2[PtCl6] and FeSO4. In this work, the following are used as reducing agents: an aqueous solution of Na2BH4 and an alkaline solution of N2H4 • H2O.

The reduction of Fe2+ [16] ions with an aqueous solution of NaBH4 occurs according to the scheme (1):

\[6\text{Fe}^{2+} + 12\text{BH}_4^- + 33\text{H}_2\text{O} \rightarrow 6\text{Fe} \cdot \text{B} + 11\text{H}_3\text{BO}_3 + 40.5\text{H}_2\]  

(1)

In work [16] it is shown that at a pH value of 1-7 the amount of boron in the target product increases. As the temperature decreases, the boron content in the reduced metal decreases. The rate of hydrolysis of the borohydride anion also decreases according to the scheme (2) [17]:

\[\text{BH}_4^- + 4\text{H}_2\text{O} \rightarrow \text{B(OH)}_4^- + 4\text{H}_2\]  

(2)

The reduction of Pt4+ with borohydride anion occurs in stages [16]. In the first stage, Pt4+ is reduced to Pt2+. Further, Pt2+ is reduced to metallic platinum (Ptº) according to the scheme (3):

\[2\text{Pt}^{2+} + \text{BH}_4^- + 3\text{H}_2\text{O} = 2\text{Pt} + \text{H}_3\text{BO}_3 + 7\text{H}^+\]  

(3)

Hydrogen released during hydrolysis (2) is adsorbed on reduced platinum [19], while BH4 is catalytically hydrogenated on its surface by reaction (4):

\[\text{BH}_4^- + \text{H}^+ = \text{BH}_3 + \text{H}_2\]  

(4)
One of the simplest ways to increase the reducing ability is a super stoichiometric ratio (20-30-fold excess) of NaBH₄ to the metal being reduced [17].

When reducing metals with hydrazine hydrate [18] according to scheme (5), molecular nitrogen is released as a by-product, which is inert with respect to the main product.

\[
2\text{Me}^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 2\text{Me}^0 + \text{N}_2 + 4\text{H}_2\text{O}. \quad (5)
\]

At the same time, there are a number of limitations associated with the formation of sparingly soluble side compounds, since the reduction must be carried out in an alkaline medium to increase the reducing ability of N₂H₄ [18]. Bivalent iron in an alkaline medium in the presence of atmospheric oxygen is oxidized according to the scheme (6).

\[
4\text{Fe}^{2+} + 8\text{OH}^- + \text{O}_2 \rightarrow 4\text{FeO(OH)} + 2\text{H}_2\text{O} \quad (6)
\]

Catalytic decomposition on the surface of platinum metal, which can proceed according to the scheme (7), can be overcome by increasing the amount of the reducing agent introduced. Oxidation of Fe²⁺ is also inhibited by an increase in the concentration of N₂H₄ in the reaction mixture.

\[
2\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2 \quad (7)
\]

2. Experimental

For research, the following reagents were used: platinum hydrochloric acid (reagent grade), iron (II) sulfate (reagent grade), sodium tetrahydroborate (analytical grade), sodium potassium tartrate (analytical grade), sodium hydroxide (analytical grade), hydrazine hydrate (analytical grade) and isopropyl alcohol (analytical grade).

As a result, 3 samples of the FePt system with an equiatomic composition were synthesized. Sample 1 was synthesized in an open thermostated (12 ± 2 °C) reactor, into which solutions of metal precursors and a stabilizer were successively introduced. The sodium tetrahydroborate solution was added by increasing the stirring speed of a mechanical stirrer. The resulting precipitate was repeatedly washed with water and then with isopropyl alcohol.

Samples of nanoparticles 2 and 3 were synthesized in an open thermostated reactor at a temperature of 95 ºС. At a constant stirring speed of a mechanical stirrer, solutions of metal precursors were added. Then, increasing the stirring rate, a reducing mixture was added - an alkaline solution of hydrazine hydrate, while the amount of the reducing mixture in sample 3 was 2 times less than in sample 2. The resulting samples were repeatedly washed with distilled water to a neutral medium, followed by washing with isopropyl alcohol.

The samples obtained were investigated by the following methods: X-ray diffraction [19] (on a Bruker D8 Advance A25 powder X-ray diffractometer); transmission electron microscopy (TEM) [20] (JEOL JEM2100 microscope); atomic emission spectroscopy with inductively coupled plasma (AES) (spectrometer iCAP 6500 DUO LA); thermal analysis (thermal analyzer NETSCH Luxx STA409PG with synchronous mass spectrometer NETSCH Aëolos QMS403C).

3. Results and discussion

A sample of FePt 1 nanoparticles reduced with NaBH₄, according to the reduction scheme (1), could be contaminated with elemental boron. In this regard, elemental analysis was carried out by the AES method, according to which the boron content is less than 0.03 wt. %, while the composition of the resulting nanoscale system can be expressed by the formula 13 mol. % Fe-87 mol. % Pt with boron impurity 0.4 mol. %. Deviation from the specified composition, where the ratio of components 1: 1 is typical for systems with a large difference in redox potentials [18], since Pt⁴⁺ is reduced much faster than Fe²⁺. In this case, in parallel with the reduction of platinum, the catalytic decomposition of NaBH₄ occurs according to the scheme (4).

In order to get an idea of the purity of sample 1 and its temperature stability, it was studied using the method of thermogravimetry combined with mass spectrometry. Analysis of the data showed that the loss during surface dehydration is 0.7 wt. %. The maximum weight loss is observed in the temperature range of 300 - 400 ° C, which can be explained by the destruction processes of the stabilizer used, which is confirmed by the data of mass spectrometry of the released products.
According to the data obtained by the TEM method, the particles of sample 1 (Figure 1) have a sphere-like shape with an average size of 13 ± 3 nm.

![Figure 1. Micrographs of Fe-Pt particles (sample 1)](image)

Figure 2 shows an X-ray diffraction pattern of sample 1. As can be seen, there are only reflections of the solid solution phase with an fcc lattice [21], while the reflections of the oxide-hydroxide phases are not recorded.

![Figure 2. X-ray diffraction pattern of the FePt system under study (sample 1) (λ = 1.9373 Å)](image)

The lattice parameter of the solid solution calculated from the data of X-ray diffraction analysis is 3.908 Å.

According to the Scherrer equation (8), the size of crystallites was estimated:

$$D = \frac{K}{\beta \cos \theta}$$

(8)

where D is the average crystallite size, nm; k is the dimensionless particle shape factor (Scherrer's constant, in the case of spherical particles, k = 0.89 [22]); λ is the wavelength of X-ray radiation, nm; β - reflex width at half height, rad; θ - diffraction angle (Bragg angle), rad. The obtained crystallite size was 10 ± 2 nm. This is comparable to the TEM data.

In the synthesis of samples 2 and 3, the main problem is the iron oxidation reaction (6). To check the presence of iron oxides in these samples, X-ray phase analysis was also performed using the obtained X-ray diffraction patterns shown in Figure 3.
Figure 3. X-ray diffraction patterns of FePt nanoparticles (samples 2 and 3) (λ = 1.9373 Å)

The X-ray diffraction patterns of sample 3 also show no reflections characteristic of the oxide phase. According to X-ray diffraction analysis, the crystal lattice parameter of the obtained FePt solid solution is 3.910 Å. The size of nanocrystallites for this sample was 13.5 ± 3 nm (sample 2) and 12 ± 2 nm (sample 3).

X-ray phase analysis of sample 2 showed that the sample contains phases of iron oxide [23] and a solid solution FePt with a lattice parameter of 3.894 Å.

4. Conclusion

When using NaBH₄ as a reducing agent in the presence of a stabilizer - sodium-potassium tartrate, FePt nanoparticles were synthesized, which have similar physicochemical characteristics to FePt nanoparticles obtained using an alkaline solution of hydrazine hydrate. The content of boron in the samples upon reduction with sodium tetrahydroborate is 0.03 wt. %. When synthesizing FePt nanoparticles using hydrazine hydrate, it was found that after the formation of a suspension of nanoparticles in the reaction medium, it is necessary to immediately remove the working solution (including the remaining reducing mixture). Because the pH of the solution medium is in the range of 10-12; when the synthesized nanoparticles are in solution, the process of oxidation of the iron-rich phase can occur. Comparison of the shape and size characteristics of FePt nanoparticles showed that the size of particles obtained using NaBH₄ as a reducing agent is smaller than particles obtained by reduction with N₂H₄·H₂O, 10 ± 2 nm and 13.5 ± 3 nm, respectively, and the crystal lattice parameter is, on the contrary, larger. 3.908 Å and 3.894 Å, respectively.

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