Transmission electron microscopy for evaluating the structural parameters of nanoparticles

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Abstract. In this work, on the example of bimetallic systems FePt and FePd, an approach is developed to assessing the structural parameters of nanoscale mono- and polymetallic systems by transmission electron microscopy (TEM), in comparison with the X-ray diffraction method of analysis. The interplanar distances, average sizes and phase compositions of FePt and FePd nanosystems are calculated.

1. Introduction
Nanosized bimetallic systems of the subclass (Fe, Co, Ni) - (Pt, Pd) have high magnetic characteristics - a record coercivity for bimetals in combination with relatively high values of saturation magnetization [1-5]. As a result, they are recognized as promising for medical applications [6, 7], as materials with superdense information recording [8], for creating subminiature permanent magnets, etc. However, the realization of these possibilities is hindered by the unsolved problems of preserving the ferromagnetic state of nanosized bimetallic particles formed in the form of a tetragonal phase L1₀ with a high degree of structural ordering up to the actual temperature range of 320-350 K in the presence of various external influences, the solution of which requires the development of methods for studying the crystal structure and phase compositions of nanoparticles at the level of individual crystallites.

The most widespread methods for obtaining this information are methods of X-ray diffraction analysis [9-15], which make it possible to determine the phase composition and perform structural analysis of a substance, as well as to estimate the size of the resulting particles. However, when carrying out this analysis method, the researcher sees an integral diffraction pattern from the surface of the object under study, while the study of separate (individual) nanoparticles is extremely difficult.

At the same time, the number of methods for assessing the shape and size and structural parameters of nanoobjects by X-ray diffraction methods is not limited [12]. In this work, an approach is made to the study of the structural characteristics of FePt and FePd nanoparticles by high-resolution transmission electron microscopy (TEM), since in this case, it is possible to distinguish between individual atoms of the crystal lattice of the objects under study.

By analyzing the micrographs obtained using a transmission electron microscope, one can calculate the interplanar distance (d) and calculate the parameters of the crystal lattice of the fcc solid solution (1) formed during the synthesis of the studied nanosystems FePt and FePd, [16].
\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2},
\]

where \(d\) is the interplanar distance, nm; \(h, k, l\) are Miller's crystallographic indices; \(a\) - lattice parameter, nm.

Knowing the value of the crystal lattice parameter, it is possible to estimate the ratio of the components in the composition of the nanosystem according to Vegard's rule [17]:

\[
a = a_1 x_1 + a_2 x_2,
\]

where \(a_1, a_2\) are the lattice parameters of the solid solution, nm; \(x_1, x_2\) - mole fractions of the corresponding components of the solid solution.

2. Experimental

In this work, we studied nanosized FePt systems obtained by the method of joint reduction of aqueous solutions of platinum (IV) hydrochloric acid and iron (II) sulfate with sodium tetrabohydride, and FePd, obtained by the method described in [18], by co-reduction of aqueous solutions of palladium chloride and iron (II) sulfate with hydrazine-hydrate (all reagents of analytical grade).

X-ray diffraction analysis of the synthesized FePt and FePd nanosystems was carried out on a powder X-ray diffractometer (Bruker D8 Advance A25) at room temperature in copper radiation (CuK\(\alpha\) radiation, \(\lambda = 1.5406 \ \text{Å}, \text{Ni filter on the secondary beam}) by the polycrystal (powder) method at the Center for Collective Use of the Federal Research Center of Coal and Coal Chemistry SB RAS. X-ray diffraction patterns were taken at long accumulation times (2 s), in the range of angles (2\(\theta\)) and scanning steps of 5–75° and 0.02°, respectively. The data obtained from the X-ray diffraction patterns were used to determine the phase composition and calculate the interplanar distances, crystal lattice parameters, and the particle size.

Photomicrographs of the particles were obtained with a transmission electron microscope (JEM2100) in bright-field recording mode; accelerating voltage 200 kV. Microdroplets of an alcoholic suspension of nanoparticles were applied to a preparative copper grid covered with a carbon layer by placing the grid in a cloud of microdroplets created using an ultrasonic homogenizer. Then, to remove traces of solvent, the samples applied to the grid were dried for several hours, after which they were washed with distilled water using a non-magnetic metal holder. In this case, magnetic nanoparticles were held on the preparative grid using a strong permanent magnet placed under the bottom of the Petri dish, in which the grid was washed. Finally, the grid with the sample was dried for a day and used in TEM experiments.

3. Results and discussion

Figure 1 shows TEM images of nanoparticles of compositions Fe\(_{0.5}\)Pt\(_{0.5}\) and Fe\(_{0.45}\)Pd\(_{0.55}\). The obtained electron micrographs were used to analyze the shape and size of nanoparticles (for each investigated object, 20 microimages of the ensemble of particles were used), and the inter-row distances were calculated. The inter-row distances and sizes of nanoparticles were calculated using the ImageJ software package [19].
Based on the data obtained, histograms of the size distribution of the studied nanoparticles were plotted, which are shown in Figure 2.

**Figure 2.** Size distribution of nanoparticles FePt (a) and FePd (b)

Analysis of micrographs and size distribution curves show that FePt and FePd nanoparticles have a spherical shape, the average diameter of which is 13 ± 3 and 10 ± 2 nm, respectively.

High-resolution micrographs make it possible to observe individual rows of atoms in the crystal lattice of a material [20]. Enlarged micrographs of individual nanoparticles make it possible to distinguish between individual regions with the most distinct atomic rows (Figure 3). The distance between the rows of atoms is a definite crystallographic parameter (depending on the angle of observation of the object under study). An example of calculating the inter-row spacing for an individual particle of the FePd system is presented in Table 1, which shows the procedure for processing data obtained by the TEM method.
Figure 3. Enlarged micrographs of nanoparticles FePt (a) и FePd (b)

Table 1. An example of calculating the inter-row spacing (using the example of an individual FePd nanoparticle)

| Number of distances between atomic layers, n | Interlayer distances d, nm | \( R_i^{(exp.)} \), nm | \( n_i R_i \), nm | \( R_i^{(calc.)} \), nm | \( \Delta R \), nm | \( (\Delta R)^2 \) |
|---|---|---|---|---|---|---|
| 5 | 0.236 | 1.180 | 25 | 5.900 | 1.199 | 0.019 | 0.000367 | 17.9546 |
| 9 | 0.240 | 2.160 | 81 | 19.440 | 2.158 | 0.002 | 0.000002 | 17.3611 |
| 11 | 0.240 | 2.640 | 12 | 29.040 | 2.638 | 0.002 | 0.000004 | 17.3611 |
| 19 | 0.240 | 4.560 | 361 | 86.640 | 4.557 | 0.003 | 0.000010 | 17.3611 |
| Sum | 784 | 188.648 | | | | | 0.000383 |

\( R_i^{(exp.)} \) are the measured distances between the extreme rows of atoms in the studied system of bands.

\( R_i^{(calc.)} \) - calculated distances between extreme rows in the studied system of strips.

\( (R_i^{(calc.)} = <d> \cdot n_i) \).

\( \Delta R \) – difference between calculated and experimental distances.

The calculation of the weighted average row spacing was determined by the formula (3):

\[
<d> = \frac{\sum n_i d_i}{\sum n_i^2},
\]

where \( n_i \) is the number of row spacings in the observed system of stripes; \( d_i \) is the calculated row-to-row distance [21]. The average distance in the studied system of bands in the FePd nanoparticle is 0.2398 nm. The standard deviation was calculated by the formula (4) according to [22]:

\[
\Delta r = \sqrt{\frac{\sum (\Delta R_i)^2}{\sum n_i^2 (N - 1)}},
\]

where \( N \) is the number of measurements.

The standard deviation is 0.00047 nm, the confidence interval is 0.00065 nm. The arithmetic mean inter-row distance in the FePt system is 0.270 nm. It is natural to compare this value with the inter-row distance in the (100) plane for platinum, which is equal to the distance between platinum atoms in the indicated plane. This distance is 0.274 nm (according to the PDF file \( a(Pt) = 3.878 \text{ Å} \) [22], which is close to that found from the TEM data. For iron with the same fcc structure, the interplanar spacing is 0.257 nm. Based on Vegard’s rule (2) and the assumption of the formation of a solid solution in the system, the concentration of iron in it is 23 at. %. This value corresponds on the phase diagram of the system to the intermetallic compound FePt3 with an fcc structure [23].
For additional analysis of the data obtained by the TEM method, the FePt and FePd samples were also investigated by X-ray structural analysis. The X-ray diffraction pattern of the FePt nanosystem is shown in Figure 4, a.

Broadening of reflections according to the Scherrer formula [24] (5):

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

where $D$ is the average crystal size; $K$ is dimensionless particle shape factor (Scherrer's constant); $\lambda$ is the wavelength of X-ray radiation; $\beta$ is reflection width at half maximum; $\theta$ is diffraction angle (Bragg angle). The estimated crystallite size was 14 ± 2 nm, which is close to the value obtained by the TEM method.

The TEM micrographs of FePd nanoparticles were used to calculate the interplanar distance, which was 0.241 ± 0.001 nm and corresponds to the interplanar distance of a family of planes (h00). The lattice parameter of the FePd nanosystem under study is 0.341 nm.

One of the most common interplanar spacings in TEM images is 0.202 nm, which corresponds to Fe(OH)$_2$ in the (100) plane, the lattice parameter is 0.326 nm.

A typical X-ray diffraction pattern of the FePd nanosystem is shown in Figure 4, b. As can be seen, only the lines of the fcc phase are recorded.

![Typical diffraction patterns of systems FePt (a) и FePd (b).](image)

**Figure 4.** Typical diffraction patterns of systems FePt (a) и FePd (b).

4. Conclusion

The method of high-resolution transmission electron microscopy can be used as a tool for assessing not only the size, but also the structural-phase parameters of individual nanoparticles. However, since only a portion of the sample under study is considered by TEM, it is almost impossible to fully assess the structure and phase composition of a nanostructured object. To do this, together with the TEM method, it is necessary to carry out X-ray structural analysis of the objects under study.

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