Cryogenic synthesis of nanodimensional magnetite

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Low temperature synthesis of single-domain magnetite particles at the liquid-solid interface was developed. Spherical particles of crystalline magnetite with sizes of 6–50 nm were prepared. Investigation of phase and element composition as well as morphology of single-domain magnetite was performed with the help of X-ray phase analysis, Auger-spectroscopy, raster electronic and atomic force microscopy.

Разработана методика низкотемпературного синтеза однодоменных частиц магнетита на границе твердой и жидкой фаз. Получены сферические частицы магнетита размером 6–50 нм. Проведено исследование фазового, элементного состава и морфологии синтезированных частиц методами рентгенофазового анализа, оже-спектроскопии, растровой электронной и атомно-силовой микроскопии.

The close attention of researchers to composites containing magnetic nanoparticles is due to the fact that those possess specific properties that are not characteristic of a solid magnetic material. The differences observed in their Curie or Neel temperatures reach hundreds of degrees. Besides, they exhibit a number of such unusual properties as gigantic magnetoresistance, anomalously large magnetocaloric effect, etc. [1].

The modern medicine is known to employ magnetic medical preparations on the basis of magnetite including, for example, radioopaque contrast agents. Thus, Belikov et al. [2] described a radioopaque contrast agent containing magnetite in a liquid carrier, namely, tetradecane. In [3], an aqueous colloidal solution of magnetite has been proposed as an efficacious haemostatic agent which is also used to visualize biologic tissues that include apoferritin (protein shell of ferritin) with magnetite crystals in its pores.

Among promising development fields of magnetic materials with extended surface, there is preperation of sorbents [4] as well as magnetosensitive nanocomposites for a guided transport of medical agents [5–9]. Magnetic therapeutic forms may contain no pharmaceutical substance, with the curative effect produced in such a case resulting from the action of a constant magnetic field (whose source is a magnetic therapeutic form by itself) or of an external high-frequency magnetic field. Topical and urgent development tasks in the modern pharmaceutics [10–13] include preparation of combined medical agents for diagnostics and therapy that are effective at a cell level and that are based on magnetic carriers. A great attention of researchers is also attracted by possibility of creating nanocomposites for viral decontamination of donor blood and plasma.

By varying sizes, shape, composition, and structure of nanoparticles, it is possible to control within some limits the magnetic characteristics of composites. However, such a control is not always possible during the synthesis of nanoparticles, so that properties of even single-type materials may vary considerably. In particular, the magnetic characteristics of ferromagnetics depend heavily on the size of particles forming their structure.

In view of the above-stated, this work is aimed at development of a procedure for synthesizing a nanodimensional magnetite with a pre-specified particle size distribu-

tion (in particular, with a narrow single-domain one).

When magnetite is used for medical purposes, its nanoparticles must comply with the following requirements. The particle size should not exceed about 60 nm (for particles to be able to go through capillaries without causing embolization); the particles should possess an adequate magnetic field sensitivity (i.e., have a sufficiently high magnetic moment) in technically attainable field range for handling the particles in the blood flow at its physiologic parameters. In the case of magnetic nanoparticles, this value coincides with a theoretical estimate of the smallest magnetic domain size for a large majority of magnetic materials. It is to note here that magnetite particles in its single-domain state possess the highest coercive force. Estimations show that at 300 K, the size of a spherical single-domain magnetite particle is about 30 nm [1]; the carriers should be able to carry a necessary set of chemotherapeutical agents; the pharmaceutical substance administrated should occupy an essential part of the preparation volume; the organism treated should not be overloaded with a magnetic material; the surface properties of carriers should provide for a maximal biocompatibility and minimal antigenicity; after performing their functions, the magnetic carriers used should undergo biodegradation, with the degradation products being readily removed out of an organism or being noted for their minimal toxicity.

The magnetite synthesis procedure should provide the material in the form of particles of specified size and shape (in any case, the distribution of sizes should not be considerable and be controllable by the synthesis conditions). The most commonly used method for synthesizing magnetite nanoparticles is the chemical condensation proposed by Elmore [14]. The method consists in a rapid neutralization of salts of bi- and trivalent iron with an excess of alkali or aqueous ammonia. In order to produce highly dispersed precipitate, it is necessary to provide conditions for intense nucleation. To that end, supersaturated solutions of salts can be used and even melts of their low-melting crystalline hydrates [15]. The particle growth rate at the nucleation stage can be lowered and adjusted by decreasing crystallization temperature, which provides the attaining and maintaining as long as possible a substantial supersaturation in separate local heterogeneous regions of a solu-

tion, which, in its turn, results in formation of numerous crystallization sites. Any local supersaturation at the nucleus growth stage can be prevented by a proper stirring of solutions. In such a case, there are no conditions for formation of new nuclei, which makes it possible to obtain particles with a narrow size distribution, to control their size and, thereby, to increase the yield of single-domain magnetite particles.

The main parameters that define the finished product properties are concentrations of starting salts and precipitating agent as well as the synthesis temperature and the mixing rate of solutions. The latter parameter of the heterogeneous synthesis is the least amenable to control, while it is of a great importance in defining the concentration gradients of starting salts in the reaction zone during the formation of magnetite nuclei and their subsequent growth. In fact, when two concentrated solutions of mixtures of different valence iron salts and precipitating agent (ammonia) are mixed resulting in appearance and growth of nuclei, the reaction of insoluble product formation proceeds at interfaces of two liquid phases. The number of a new phase nuclei and the structure of the formed crystals depend on concentration gradients of the starting salts. To preset and monitor the desired concentration gradient of starting constituents as well as to maintain it constant in the solution for a certain period of time is a rather difficult technological task. During the mixture stirring and formation of the reaction products, the concentrations of starting constituents in the nearest surrounding of the reaction product decrease (down to the equilibrium values characteristic of the specified temperature and concentrations at the heterogeneous interface saturated solution/solid magnetite), thus resulting in cessation of new nuclei formation and in growth onset of separate particles under conditions more close to the equilibrium ones. To set rather severe conditions of synthesis and to increase concentrations of salts in the initial aqueous solution, some researchers [15] resort even to increasing of the synthesis temperature up to 315 K (melting point for the crystal hydrate). In this case, the nucleation and growth of crystals proceed in conditions that vary in the course of one and the same synthesis. The material prepared in this way is noted for a considerable scatter in its main parameters (particle size distribution, degree of crystallinity, physical char-
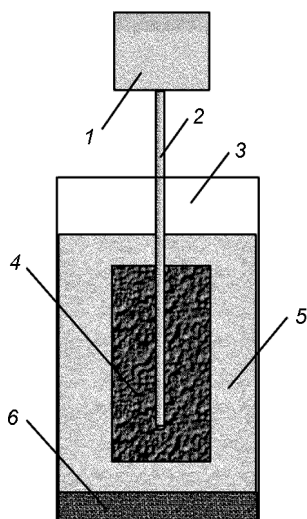
Fig. 1. Block diagram of a setup for cryogenic synthesis of monodomain magnetite.

Fig. 2. Dependence of freezing temperature T of the salt solution A on water volume fraction X_{H_2O}.

acteristics). To attain the purpose specified above, it is necessary to maintain constant values of the appropriate temperature and concentration gradient of constituents in the reaction zone.

The above-stated conditions necessary to provide a stable predictable result may be realized in the heterogeneous synthesis of magnetite at interfaces of a solid phase (frozen solution of salts) and liquid phase (excess of ammonia solution at a fixed concentration). During the melting of the salt solution, it is possible to maintain a constant (as a first approximation) concentration gradient at the thin phase interface layer. On the one hand, there is an excess of ammonia solution, while on the other hand, the solid phase melting provides a solution with a pre-specified constant concentration of reaction components which is involved in the reaction. In contrast to the heterogeneous synthesis, the growth of nanoparticles stops at some distance from the frozen salt solution surface due to the essential absence of the iron salt. This makes it possible to prevent any uncontrolled growth of the formed particles and to preserve their primary size.

The endothermic process of the salt solution melting under the solid ↔ liquid equilibrium conditions provides the constant temperature in the reaction zone, thus promoting formation of nanodimensional particles with a close size distribution. It is also evident that the low temperature of the reactive suspension inhibits any aggregation of near-critical nuclei and their subsequent recrystallization that would result in formation of large particles with undesired structurization.
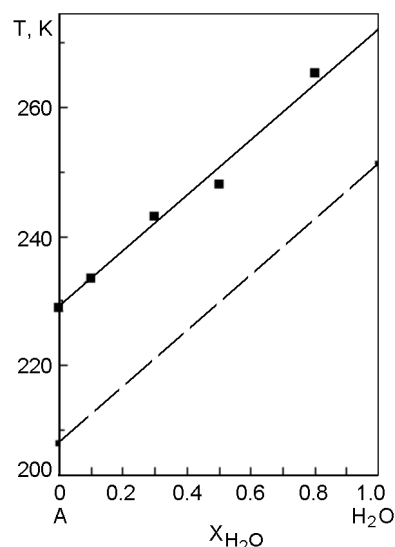
As to the the reactor (Fig. 1) design, it consists of a beaker (*3*) containing ammonia solution (*5*) and a fluoroplastic rod (*2*) with a frozen cylinder of the salt solution (*4*) of a certain composition at one end immersed into the ammoniac solution while the rod second end is fastened to the rotor of a motor (*1*). The magnetite (*6*) formed due to the reaction is precipitated at the beaker bottom.

Magnetite nanoparticles were synthesized as described lower. Iron sulfate $FeSO_4 \cdot 7H_2O$ was dissolved in the minimal amount of water (26.3 g per 100 g H_2O at 293 K). The stoichiometric amount of ferric chloride was heated up to 315 K and poured under stirring into the previous solution. The mixture obtained was a concentrated solution of iron salts (A). Then, some amount of solution A and water at a certain ratio in a thin plastic beaker was cooled down to a temperature by about 20 K lower than the crystallization point of the mixture at the preset composition (Fig. 2, dashed line). The desired cooling was attained with the help of rod 2 (of a low thermal conductance) inserted into the plastic beaker. After freezing, the plastic beaker was removed by heating it in a water bath. The rod 2 was attached to the motor rotor and then the frozen salt solution cylinder was immersed into ammonia solution of an appropriate concentration. The rotation speed was about 200 rpm. The cylinder thawing resulted in formation of the salt solution of a pre-specified concentration that reacted with the ammonia solution to form a highly disperse magnetite.
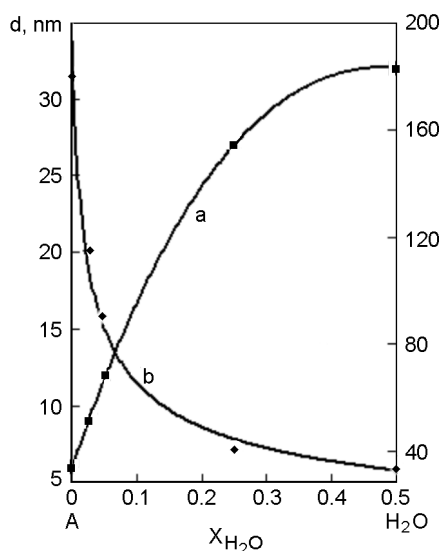
Fig. 3. Dependence of the magnetite particle average diameter and the powder specific surface area (a and b, respectively on the water dilution extent of concentrated solution A) (X_{H_2O} - volume fraction of H_2O).
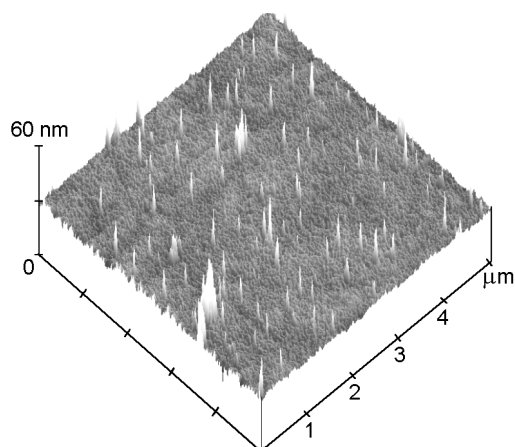

Fig. 4. Diameter distribution of magnetite nanoparticles.

Fig. 5. AFM image of nanodimensional magnetite particles on polished surface of silicon single crystal.
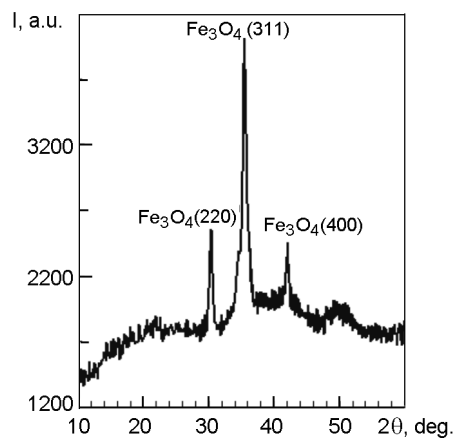
Fig. 6. X-ray powder diffraction of nanodimensional magnetite.

The magnetite was precipitated using a constant magnetic field and then the solution was decanted. The magnetite precipitate was repeatedly washed to remove all the anions present in the solution.

Following the above-described procedure, we have prepared samples of spherical particles of crystalline magnetite. The specific surface area of the dried powder measured by the argon adsorption method was within the interval of 40–180 m^2g^{-1} (Fig. 3). Depending on the synthesis conditions, the particle size were within limits of 6 to 50 nm; the particles were noted for a very narrow size distribution (Fig. 4).
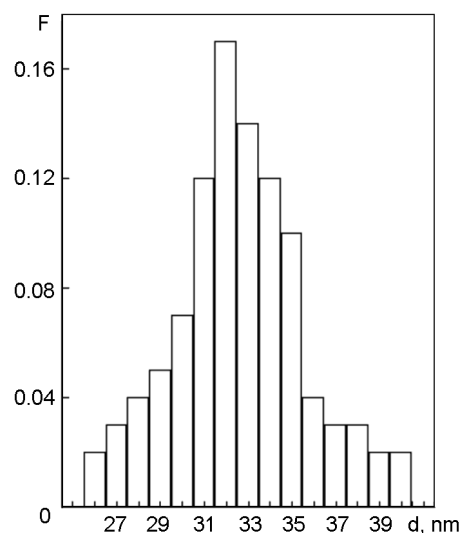
We have also determined the conditions necessary to prepare a monodomain magnetite, with the *in situ* control of the particle size realized using a Digital Instruments NanoScope force nanoscope (Fig. 5). The presence of a crystalline structure was confirmed by X-ray diffraction (Fig. 6) and measurements of magnetic characteristics.

The procedure proposed provides a number of advantages. It makes it possible to effect a direct synthesis of monodomain magnetite particles at a high yield, to spend economically the starting reagents, and to simplify the subsequent separation of a highly dispersed product.

Thus, the developed synthetic procedure provides the preparation of nanodimensional magnetite particles at solid/liquid phase interfaces at a predicted yield of a large frac-

tion of particles of a pre-specified size (in particular, of monodomain particles). Some structural and physical properties of highly dispersed magnetite have been studied depending on the synthesis conditions.

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Кріогенний синтез нанорозмірного магнетиту

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Запропоновано низькотемпературну методику синтезу однодоменних частинок магнетиту на границі твердої та рідкої фаз. Одержано сферичні частинки магнетиту розміром 6–50 нм. Проведено дослідження фазового, елементного складу та морфології синтезованих частинок методами рентгенофазового аналізу, оже-спектроскопії, растрової електронної та атомно-силової мікроскопії.