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The structural and morphological study of the powder sample of strontium hexaferrite

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In the paper the results of X-ray diffraction and electron microscopic examination of the ferrite sample are presented. It is found that the ferrite consists of particles with size of 20-50 nm, with a narrow size distribution. It has been shown that the individual ferrite particles tend to unite in large complexes, with an average size of 600 nm. A complex structure of hexaferrite particles was detected, which consists of a dense core and a light shell.
Keywords: ferrite, X-ray diffraction, powder particle size.

В работе представлены результаты рентгенографического и электронно-микроскопического исследования ферритового образца. Установлено, что феррит состоит из частиц размером 20–50 нм с достаточно узким распределением по размерам. Показано, что отдельные частицы феррита стремятся объединиться в крупные комплексы, средний размер которых составляет 600нм. Обнаружена сложная структура частиц гексаферрита, которые состоят из плотного ядра и более легкой оболочки.
Ключевые слова: феррит, рентгенограмма, размеры частиц порошка.

У роботі представлені результати рентгенографічного та електронно-мікроскопічного дослідження феритового зразка. Встановлено, що ферит складається з частинок розміром 20-50 нм з досить вузьким розподілом за розмірами. Показано, що окремі частинки фериту прагнуть об'єднатися у великі комплекси, середній розмір яких становить 600нм. Виявлена складна структура частинок гексафериту, які складаються з щільного ядра і легшої оболонки.
Ключові слова: ферит, рентгенограма, розміри частинок порошку.

It is well known that modern electronics development is moving towards increasing the density of the elements. This inevitably leads to the necessity of using in electronic devices of components that have increasingly smaller sizes. However, many of their physical properties depend on the size, and may vary with time. The reason for this can be both chemical interaction processes and diffusion processes which are substantially more active in nanoscale samples than in the bulk ones [1]. Thus, the study of the properties of fine materials, as well as using them as technological objects or model samples, is impossible without a thorough study of their morphology.

This work is devoted to the study of the structure of strontium hexaferrite $SrFe_{12}O_{19}$, which is a hard magnetic material and an important component for the manufacture of magnets, which is applied in many fields of technology: from the carriers in recording devices to medical and biological innovations. Due to the wide application, ferrites are investigated in considerable detail. However, to evaluate the influence of particle size on physical properties, particularly, magnetic properties, it is necessary to understand how the morphology of ferrite powders changes with an increase of dispersity and, consequently, with the rise of the contribution of the surface, and also to have samples with reliably defined structural parameters.

It is known that the surface energy of the phase (the phase boundary) is higher in comparison with the volume energy. The energy lowering is due to the surface restructuring because of the migration of atoms or the adsorption of additional components. For example, in the study of single crystal of barium hexaferrite $BaFe_{12}O_{19}$ [2] by X-ray photoelectron spectroscopy it was found the difference between the element composition of the surface and the stoichiometric composition. On the surface there was an excess of oxygen, and positions of iron appeared to be vacancies. Such deformation of the structure leads to the distortion of the magnetic subsystem of ferrite, the depth of which, according to the authors, is less than the crystallographic one. Because of the smallness of this layer it was not detected for a long time, and the near-surface region was considered as "magnetically-dead" (non-magnetic). are obtained [3] Direct evidence of the

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existence of the surface region with "chamfered" magnetic structure of finite thickness (from 5-10nm in ferrite base compositions to ~ 200nm in aluminum substituted ferrites) was obtained from the studies [3] of the Mössbauer spectra of ferrite single crystals, that is a consequence of the existence of the surface as a structural defect. The Curie temperature of the open surface layer appears to be a few dozens of degrees (50-75K) lower than that of a bulk crystal.

During the transition from macrocrystals to nanocrystals of $BaFe_{12}O_{19}$ magnetic structure is transformed. The thickness of the plate-ferrite particles having a hexagonal shape becomes comparable with the size of magnetically perturbed area. It is accompanied by a significant decreasing of the magnetization [4.5]. In addition, by the temperature dependence of the specific magnetization, the transition from the magnetically-stable state to the superparamagnetic state in calcium-barium hexaferrite (10-60nm particle size) is detected [6].

Experimental technique

As the samples for the research, the industrial strontium hexaferrite $SrFe_{12}O_{19}$ was used. The study of the phase composition was carried out by X-ray diffraction measures using X-ray diffractometer DRON-2. This is a classical method which makes it possible to carry out a qualitative phase analysis, identification of chemical elements and compounds, studying of preferred orientation in crystals, and grain size evaluation. The morphology of ferrite samples was studied with a scanning electron microscope (SEM) JEOL JSM840 and transmission electron microscope (TEM) 100BR EME.

In additin, the possibility of transition of particles to the superparamagnetic (SPM) state was assessed by calculating the critical superparamagnetic volume of ferrite particles. Experimental research of the magnetic state in a wide temperature range was carried out by the method suggested in [8].

Samples for X-ray studies were prepared by pressing industrial strontium hexaferrite powder in a cylindrical tablet with the radius of about 5 mm and the height of about 3. For the samples examined by transmission electron microscopy (TEM), the structural basis was the carbon film that was condensed under vacuum (10^{-6} mm Hg) to a cleavage of single crystal KCl. Then the salt crystal dissolved in water and the carbon film was transferred to an electron-microscopic mesh. A drop of slurry from the ferrite powder with distilled water was applied to the prepared mesh, and then the sample was dried.

Results and its discussion

Fig. 1 shows the SEM micrograph of the investigated sample of hexaferrite. When X-ray studying the samples, it was found that they really are the single phase strontium

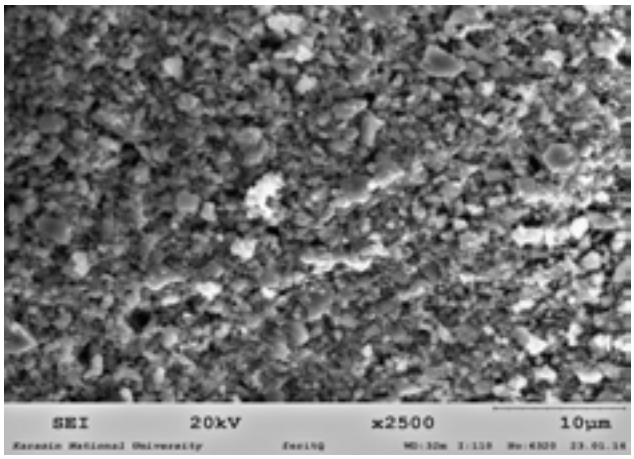

Fig.1. An electron micrograph of the pressed sample of strontium hexaferrite.

hexaferrite. The resulting Debye pattern was shown in Fig. 2. The unit cell has a hexagonal symmetry, characterized by the space group P63/mmc. The calculated lattice parameters for strontium hexaferrite $SrFe_{12}O_{19}$ are: a = 5,883 nm, c = 23,046 nm (reference: a = 5,886 nm, c = 23,037 nm). As a reference, we used data of «1996 JCPDS – International Centre for Diffraction Data. All rights reserved». It should be noted that when comparing the experimental data with the reference x-ray data, a relative change in intensity of lines (107) and (114) was found, which may be caused by the presence of a partial texture of the sample.

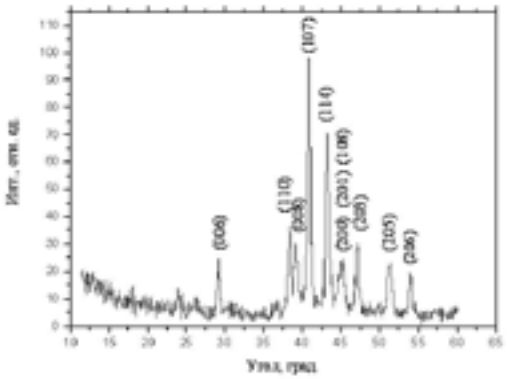

Fig.2. The XRD pattern obtained from the pressed sample of strontium hexaferrite.

The estimation of the mean characteristic size of coherent scattering regions has been made on the basis of the broadening of diffraction lines, using the Selyakov - Scherrer formula

$$D = nd = \frac{\lambda}{\beta \cos\theta} \qquad (1)$$

β is the half-width of the line; λ is the wavelength; θ is the diffraction angle; D is the crystallite size; n is the number of interplanar spacings d_{hkl}

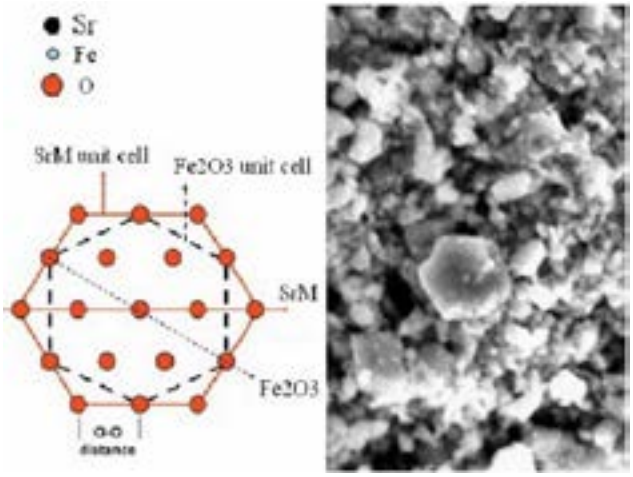

Fig.3. An electron micrograph of the strontium hexaferrite pressed sample (b) and the structure of the basal plane (a).

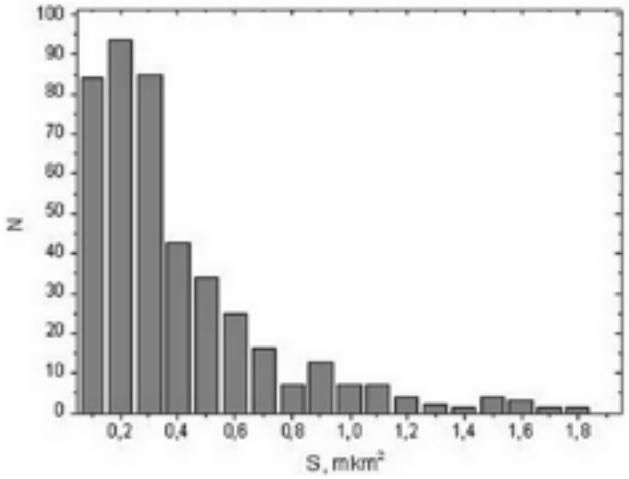

Fig.4. The histogram of size distribution of the ferrite particles.

The obtained value was equal to 20 nm. It can be assumed that the actual grain size significantly differed from this one, because the technology of obtaining powder did not provide the desired formation of nano-sized particles.

To estimate the actual grain size of the powder electron microscopy data were used. SEM image of the sample is shown in Figure 3. In the photo it is clearly visible the particle with hexagonal faceting that is typical for hexagonal symmetry P63/mmc.

Determination of the average typical size of particles observed in the pictures, and the construction of their size distribution were carried out using specially designed software. The resulting distribution is shown in Fig. 4 [9].

The average crystallite area according to research data was S = 0,370 mkm^2, which corresponds to the average typical size D = 600nm. This significant difference between the results of X-ray analysis and SEM suggested that the particles observed in Fig. 1, 3 have composite structure, and the process of pressing samples and relatively low resolution of SEM complicate their fine structure observation, for registration of which the methods of transmission electron microscopy were used.

In the picture (Fig. 5) obtained at low magnification, the general structure of the sample is shown. Ferrite particles come together in fairly large complexes, which are elongated structures having length many times greater than their transverse dimension. Such aggregation of the particles of the ferrite powder is, probably, due to the strong uniaxial magnetocrystalline anisotropy of hexaferrite, which determines the tendency of the particles to unite. The sizes of such composite particles are in the range from

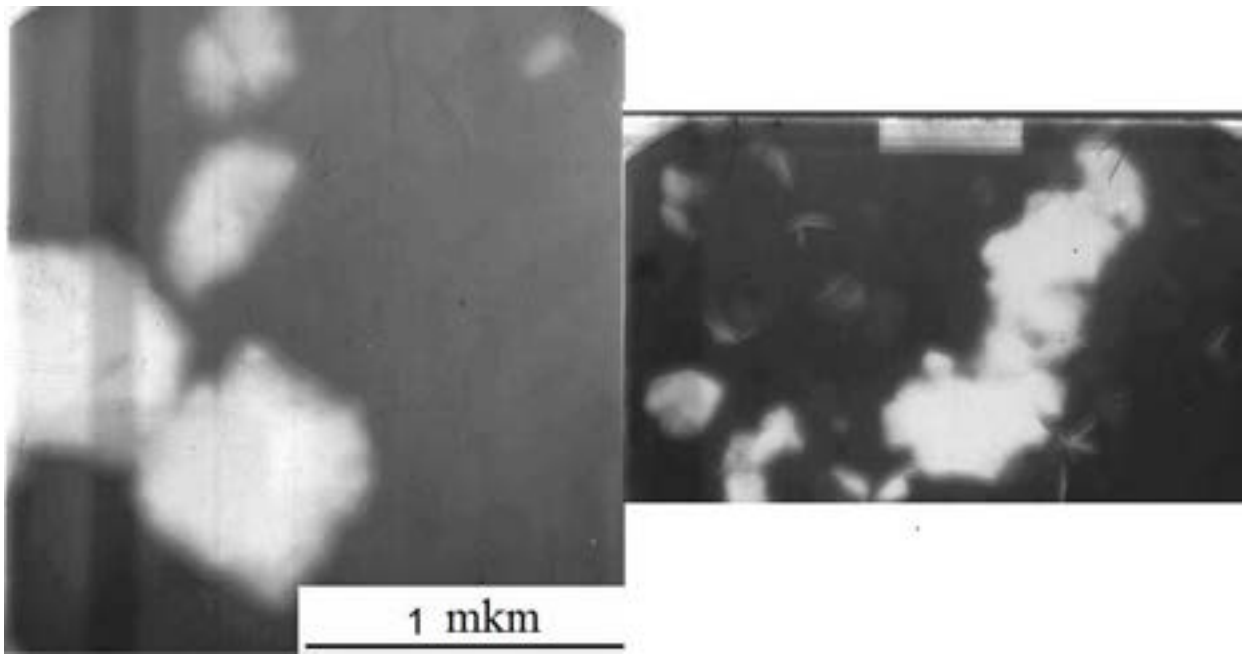

Fig.5. Illustration for composite structure of particles of studied sample.

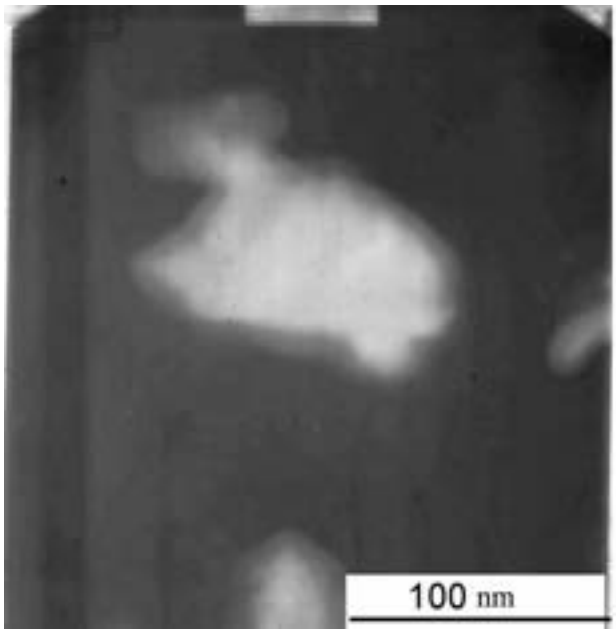

Fig.6. complicated structure of individual particle at high magnification.

about 200 nm to 8000 nm, and in some pictures even larger units are detected. Averaged value of the typical size of such composite particles is about 600 nm and coincides with the results obtained with the use of SEM.

In addition to the large composite particles, complicated structure of which is clearly visible in the fluorescent screen of electron microscope, there are a small number of particles having much smaller size. Besides small size, these particles are characterized by narrow size distribution. Particles of this class have a typical size in the range of 25-50 nm that is comparable to the value obtained during radiographic examinations.

A similar pattern was observed in [7] in the study of nanocomposite WC-Co alloy. Evaluation of grain size on the X-ray data (50nm) basis gave about 1000 times smaller result than the SEM (75mkm). However, these large friable particles were easily crumbled by grinding into smaller nanocrystalline grains, the size of which according the TEM data correlated with X-ray data.

Furthermore, the analysis of electron microscopic images showed that the nano-sized particles of ferrite have a complex structure as well, and consist of fairly dense core surrounded by lighter shell which is more transparent for the electrons (Figure 6). The depth of the shell is about 10

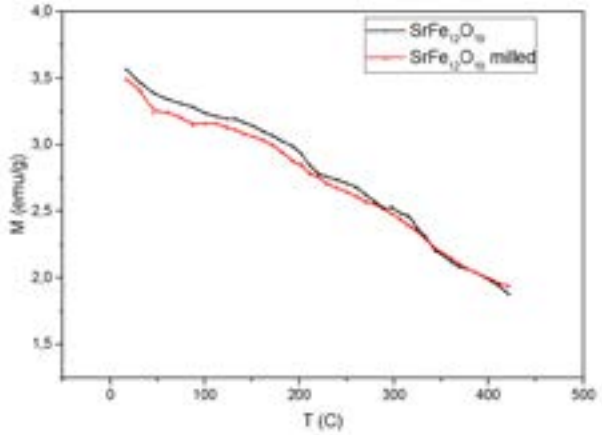

Fig.7. Temperature dependence of magnetization at constant external field H=1 kOe.

nm. This result agrees with the results of [2] which indicate the difference between the surface and the stoichiometric structures. According to the authors, on the surface there exist an excess (compared to stoichiometric) amount of lighter and hence more “transparent” oxygen ions and deficit of relatively heavy iron.

The possibility of transition of the particles of investigated hexaferrite system $SrFe_{12}O_{19}$ into the SPM state is found out by evaluating the critical superparamagnetic volume $V_{so}(H = 0)$ and comparing it with the actual minimum volume V_{min} obtained by microscopy.

The critical volume is determined by equating the magnetic anisotropy energy of the particles and thermal energy [8]:

$$KV_{so} = 25kT \qquad (2)$$

It is evident that with temperature increasing the magnitude of critical volume rise substantially, and thus the probability of the transition of particles in to the SPM state grows.

As can be seen in the curves of σ (T) (Fig. 7) taken at a fixed magnetic field H = 1 kOe, the anomaly predicted by Pfeiffer [4] is not observed. This indicates that actual particles volume is above the critical superparamagnetic one all over the temperature range up to the Curie temperature. It can be assumed that a slight part of the powder with small particle sizes, which was detected in micrographs, goes into SPM state. However, in view of the small pro rata contribution of this group of particles, the anomaly in

Table 1.

The dependence of the magnetocrystalline anisotropy constant and the critical volume of the particles on temperature

T	K_1 *10^{-6}, ergs / cm^3	$K_1(T)/K_1(300)$	V_{S0}*10^{-21}, cm^3	d_S, nm
300	3.3	1	279	11.2
400	2.7	0.818	455	13.2
500	2.04	0.618	752	15.7
600	1.23	0.373	1501	19.7
700	0.24	0.073	8944	35.7

the temperature dependence of the magnetization does not occur.

Conclusions

In this paper it is founded that the ferrite used for radiographic studies, has a hexagonal structure. Redistribution of intensities of the diffraction lines indicates the texturing of the sample, which is confirmed by TEM studies. By SEM research it is revealed that the morphology of the molded ferrite samples is represented by a number of large particles having a typical size of about 600 nm. It was found that the ensemble preserves magnetically stable condition over the entire temperature range, up to the Curie point, despite the presence of the fraction of particles whose dimensions match the SPM transition condition, which generally correlates with the results of microscopic research. At the same time, TEM studies have shown that these particles have a complicated structure and are composed of separate units, distributed in a narrow range of sizes, and their average size is about 45 nm and generally correlates with the diffraction analysis results. Furthermore, a complex structure of separate ferrite particles is determined. It was first found by TEM that the particles consist of a massive core surrounded by a lighter shell.

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