MAGNETIC PARTICLES
AND NANOCRYSTALLINE MATERIALS

Mössbauer and Magnetic Study of Microspheres Extracted from Fly Ashes of Power Stations[1]

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Abstract—Phase composition of six narrow size fractions of microspheres extracted from fly ashes of Ekibastuz coals has been determined by Mössbauer spectroscopy. The basic phase is defect magnetite substituted by Al, Mg, and Ti ions. The magnetic properties of microspheres depend on the content of iron and its distribution over spinel positions.

1. INTRODUCTION

Practically all ashes obtained as a result of burning coals on thermal power stations contain magnetic glass microspheres. The combination of magnetic properties and the high thermal stability of these microspheres allows one to use them as high-technology materials, such as functional components, composites, magnetic adsorbents, and catalysts. In this work, we investigated the electronic state of iron and its distribution in various phases and over crystallographic positions by Mössbauer spectroscopy in combination with thermodynamic calculations of phase composition and magnetic measurements with the purpose to clarify the mechanisms of the formation of magnetic properties of microspheres.

2. EXPERIMENTAL

Six close-cut fractions of magnetic microspheres with the contents of common iron oxide Fe_2O_3 from 36.3 up to 71.3 wt % have been extracted. Mössbauer measurements were carried out with a Co^{57} (Cr) source. The thickness of the samples studied is 5–10 mg/cm^2 under the natural contents of iron. The values of the isomeric chemical shifts are given relative to metallic iron α-Fe. The interpretation of spectra is carried out in two stages. Using the favorable fact that the values of the isomeric shifts are separated distinctly on the velocity (~0.3 mm/s for Fe^{3+}, ~0.7 mm/s for $Fe^{2.5+}$, and ~1 mm/s for Fe^{2+}), the Mössbauer spectrum is represented by the sum of groups of sextets and doublets with these values of the isomeric shifts and natural widths of lines. At the first stage, distribution functions of probabilities of the

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[1] The text was submitted by the authors in English.

hyperfine magnetic field $P(H)$ and quadrupole splitting $P(QS)$ for various valence states of iron are determined. This information has a qualitative character, since common values of isomeric shifts and quadrupole splittings for groups are used upon fitting. At the second stage, the number and rough values of the hyperfine-structure parameters of nonequivalent positions of iron are determined from the positions of the maxima and other features in the $P(H)$ and $P(QS)$ functions. This information is used to construct a model spectrum for fitting to the experimental spectrum by varying the entire set of hyperfine-structure parameters within the framework of the least-squares method. The calculation of the phase composition is carried out on the basis of the chemical-analysis data of close-cut fractions of microspheres with the help of the Melts.v2.04 program within the framework of the model of regular solutions. The saturation magnetization and the remanent magnetization are measured from hysteresis loops.

3. RESULTS AND DISCUSSION

The room-temperature Mössbauer spectra are shown in Fig. 1 for fractions of microspheres with the various contents of common Fe_2O_3 equal to 36.3, 39.3, 41.3, 49.3, 59.8 and 71.3 wt % marked by numbers from 1 to 6, respectively. The spectra are the superpositions of several sextets and doublets.

The $P(H)$ functions obtained for groups of sextets with isomeric shifts from 0.25 to 0.28 mm/s characteristic of Fe^{3+} for the different iron contents are shown in Fig. 2a. For comparison, the functions for Fe^{3+} in Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3 are also given. In the curves for microspheres, a number of features are visible. The $P(H)$ functions for groups of sextets with iso-
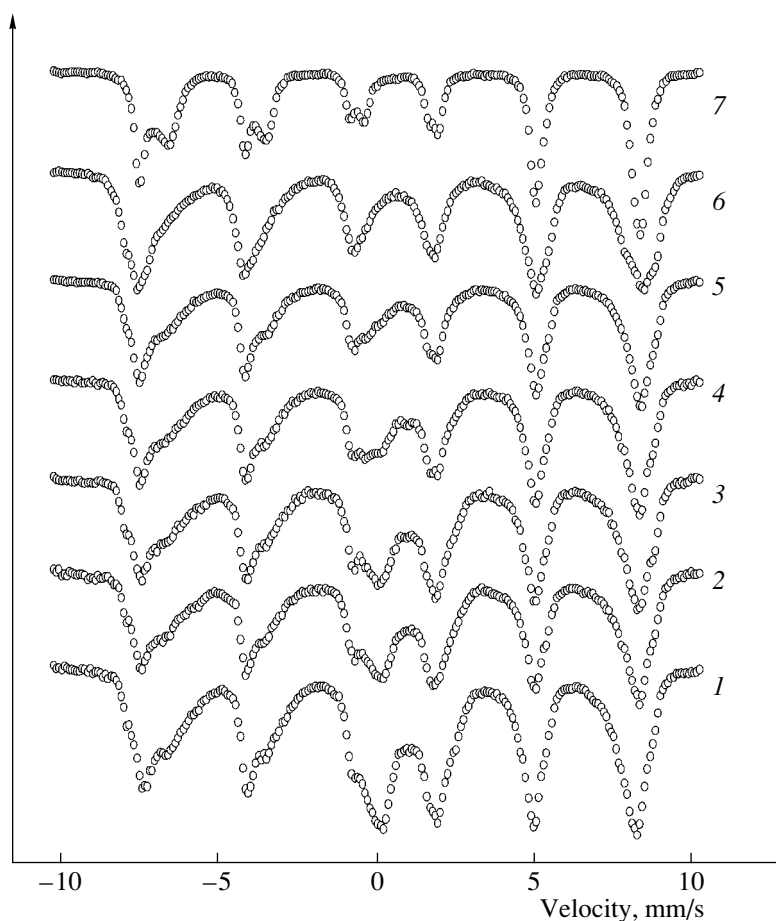
Fig. 1. Mössbauer spectra of magnetic microspheres containing (*1*) 36.3, (*2*) 39.3, (*3*) 41.3, (*4*) 49.3, (*5*) 59.8, and (*6*) 71.3 wt % Fe_2O_3; (*7*) natural Fe_3O_4.

meric shifts from 0.58 to 0.72 mm/s characteristic of mixed-valence ions $Fe^{2.5+}$ are given in Fig. 2b. For comparison, the function for $Fe^{2.5+}$ in natural magnetite Fe_3O_4 is also given. A strongly pronounced structure is seen in the distribution functions for microspheres. The divalent state of iron in the magnetic part of the spectra has not been found out.

In Fig. 2c, $P(QS)$ functions are shown for the paramagnetic part of the spectra for groups of doublets with isomeric shifts from 0.25 to 0.36 mm/s, i.e., for Fe^{3+} in a paramagnetic state at room temperature. The maxima in the functions indicate that there are a few local nonequivalent environments with a different degree of distortion. In Fig. 2d, the $P(QS)$ functions for groups of doublets with isomeric shifts from 1.06 to 1.18 mm/s, i.e., for Fe^{2+}, are given. Doublets of $Fe^{2.5+}$ are not found out. The parameters of the hyperfine structure of Mössbauer spectra obtained as a result of fitting at the second stage of their decoding are shown in the table for the sample with 36.3 wt % Fe_2O_3 as an example. In the table, only the parameters of nonequivalent iron positions having population more than 3% are given. In the magnetic part of the spectra, three crystallographic phases and two valence states of iron are found. The

basic phase is a spinel phase in which from 65 to 75 at. % common iron are concentrated. This phase is formed on the basis of magnetite. The admixture phases of hematite α-Fe_2O_3 and an alloy such as Fe(Si,Al), designated in the table as FeSi are found in all the fractions. In the paramagnetic part of the spectrum, two crystallographic phases and two valence state of iron are found. These are the spinel phase in a superparamagnetic state, Fe^{3+}(SP), and two crystallographic positions of orthosilicate or silicate clusters, M1 and M2.

The referring of iron to a concrete phase, position, and state is made based on the values of the isomeric shifts, hyperfine fields, and quadrupole splittings at the nucleus of iron [1, 2]. Of course, we understand, that this referring is formal and means only that the local surroundings in microspheres is close to the local surroundings in the specified substances.

Using results of thermodynamic calculations and Mössbauer experiment, we determined the cation distribution on the nonequivalent crystallographic positions of all atoms belonging to spinel. The amount of Fe^{3+} in octahedral positions of spinel increases and the amount of Fe^{3+}(Å) decreases (Fig. 3, curves *1* and *2*,
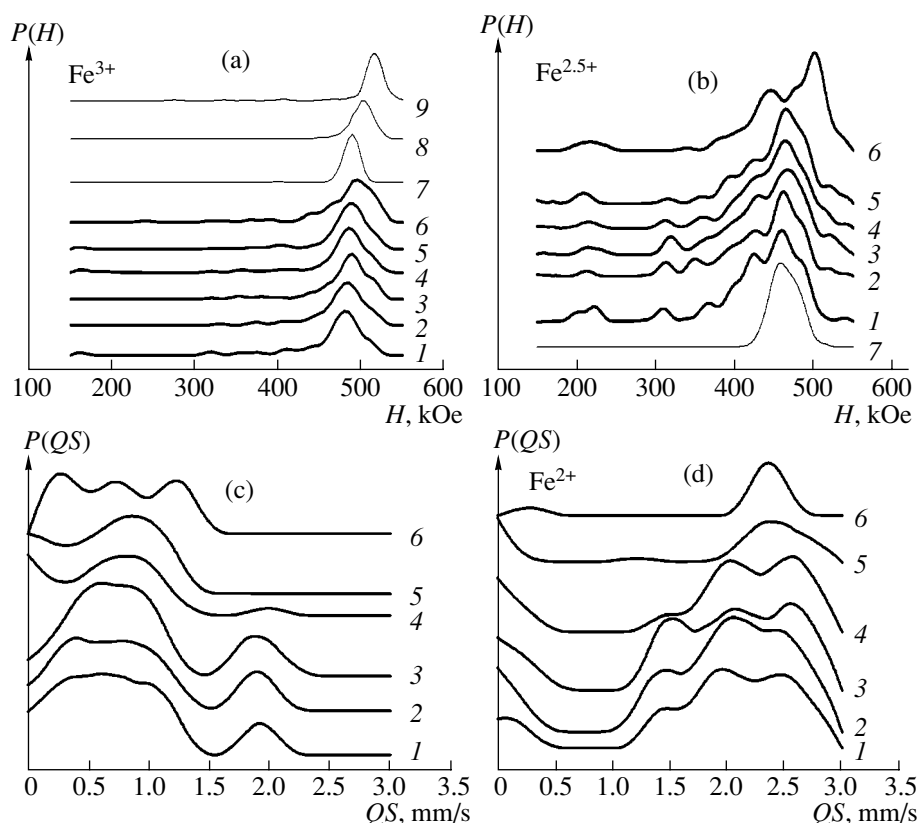
Fig. 2. Probability distributions of the hyperfine field for (a) Fe^{3+} and (b) $Fe^{2.5+}$, and of the quadrupole splitting for (c) Fe^{3+} and (d) Fe^{2+} in microspheres with different Fe concentrations; (*1–6*) same as in Fig. 1. In (a) (*7*) Fe_3O_4, (*8*) γ-Fe_2O_3, and (*9*) α-Fe_2O_3. In (b) (*7*) Fe_3O_4.

respectively) with increasing iron content. The amount of mixed-valence cations increases with increasing iron content (Fig. 3, curve *3*). Exceptions are observed for the minimum-size microspheres and for the maximum content of iron, in which case the amount of Fe^{2+} in spinel sharply falls, probably, as a result of oxidizing conditions and size effects.

Three nonequivalent positions of the mixed-valence iron are found. The presence of nonequivalent B positions in substituted spinels is usually attributed to the various number of magnetic A neighbors. The hyperfine-field change at the nucleus of $Fe^{2.5+}$ for one diamagnetic neighbor is 27–38 kOe at room temperature, which considerably exceeds values known from the lit-

The Mössbauer parameters for microspheres with 36.3 wt % Fe_2O_3. IS is the isomeric shift relative to α-Fe, ±0.02 mm/s; H is the hyperfine field, ±5 kOe; QS, the quadrupole shift, ±0.04 mm/s; W, the line width, ±0.02 mm/s; and S, the position population, ±0.05

IS $\pm$ 0.02, mm/s	$H \pm 5$, kOe	QS $\pm$ 0.04, mm/s	$W \pm$ 0.02, mm/s	$S \pm$ 0.05	Belonging to
0.38	510	−0.40	0.27	0.05	α-Fe_2O_3
0.32	484	−0.01	0.52	0.24	Fe^{3+}(A)
0.44	466	−0.29	0.75	0.17	Fe^{3+}(B)
0.68	448	−0.02	0.63	0.12	$Fe^{2.5+}$(B1)
0.64	413	0	0.79	0.09	$Fe^{2.5+}$(B2)
0.52	381	0.02	0.26	0.03	$Fe^{2.5+}$(B3)
0.02	267	0.93	0.26	0.05	FeSi
0.25	0	0.51	0.69	0.06	Fe^{3+}(SP)
0.92	0	1.82	0.58	0.06	M1
0.96	0	2.51	1.14	0.10	M2
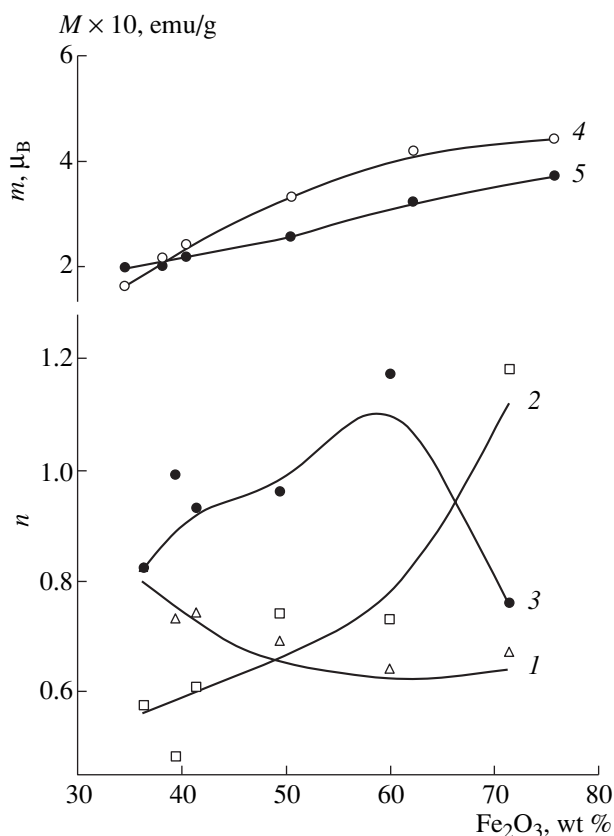
Fig. 3. Number of (*1*) $Fe^{3+}(B)$, (*2*) $Fe^{3+}(A)$, and (*3*) $Fe^{2.5+}(B)$ cations per formula unit; (*4*) magnetic moment *m* per formula unit; and (*5*) saturation magnetization *M* as functions of the Fe content in microspheres.

erature for Fe^{3+} and Fe^{2+}. It is probably that the pair of ($Fe^{3+} \longleftrightarrow Fe^{2+}$) cations "feels" features of the local surroundings to a much greater degree because of pair symmetry.

Curve *4* in Fig. 3 displays the difference of iron moments in octahedral and tetrahedral positions as the magnetic moment per spinel formula unit. The concentration dependence of the specific saturation magnetization *M* is given in Fig. 3 (curve *5*). The dependences of the magnetic moment obtained from Mössbauer and magnetic measurements coincide qualitatively. This proves that the magnetic properties of microspheres are determined by the spinel phase basically. The increase

of the microsphere magnetization with increasing iron content is caused by two factors: by increasing amount of the spinel phase and by increasing number of magnetically active cations in the octahedral sublattice as a result of a cation redistribution. With increasing concentration of the ferrimagnetic spinel phase in microspheres, the coercive force decreases from 190 Oe to 90 Oe. The remanent magnetization varied only a little and is equal to 5 ± 0.5 emu/g.

According to [4], the size of superparamagnetic spinel formations may be less than 80 Å. No mixed-valence iron $Fe^{2.5+}$ was found in the superparamagnetic phase. The critical size of 80 Å suggests that for spinel particles of up to 10 lattice parameters in size the equality of energies of the Fe^{3+} and Fe^{2+} ions of the neighboring coordination octahedrons is broken.

4. CONCLUSIONS

Despite the approximate character of the information obtained, the results of research by Mössbauer spectroscopy and thermodynamic calculations give a certain overview of the microstructure of magnetic microspheres and states of iron. We revealed that the basic iron-bearing phase of microspheres is a spinel with a defect substituted magnetite composition. A small part of this phase at room temperature is in the superparamagnetic state caused by nanosized formations of spinel. The minor phases of microspheres are represented by hematite and iron in the form of an alloy such as FeSi. The paramagnetic divalent iron is identified in the composition of orthosilicates or fragments of silicate structures. It is shown that an increase in the magnetization is caused by two contributions: an increase in the content of the spinel phase and an increase in the amount of magnetically active B cations as a result of a cation redistribution that occurs with increasing iron content in microspheres.

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