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Micromagnetic modeling of $Fe_3O_4-Fe_{3-x}Ti_xO_4$ composites

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Theoretical modeling of the magnetic properties of $Fe_3O_4-Fe_{3-x}Ti_xO_4$ composites obtained by the sol-gel method with subsequent hydrothermal treatment has been carried out. The magnetization reversal fields and the number of particles in different magnetic states of an ensemble of two-phase particles with an infinitely thin boundary between the phases and a characteristic size varying in the range from 30 to 80 nm were calculated using the „magnetic rectangles" method. Hysteresis characteristics of an ensemble of chemically inhomogeneous magnetostatically interacting particles were obtained, consistent with experimental data.

Keywords: Composites, magnetic granulometry, micromagnetism, two-phase particles, magnetostatic interaction.

1. Introduction

Theoretical studies of small ferrimagnetic particles often use the approximation of „noninteracting particles" and the assumption of their chemical uniformity (see, for example, [1,2]). The works of authors of [3,4] studied the synthesized composites $Fe_3O_4-Fe_{3-x}Ti_xO_4$ and showed that it was impossible to reconcile their magnetic properties without taking into account the heterophase of individual particles and the magnetostatic interaction between them.

In this paper, the hysteresis characteristics of $Fe_3O_4-Fe_{3-x}Ti_xO_4$ composites are theoretically calculated using micromagnetism and computer simulation methods based on the model of an ensemle of chemically inhomogeneous magnetostatically interacting particles.

2. Materials and their magnetic properties

Composite synthesis based on $Fe_mO_n-TiO_2$ system was obtained by depositing magnetite into the powder suspension TiO_2 [3,4]. 4 g $FeCl_3 \cdot 6H_2O$ and 2 g $FeSO_4 \cdot 7H_2O$ (molar ratio 2 : 1) were dissolved in 100 ml of distilled water. Then (0.5, 1 and 2 g) TiO_2 powder was dispersed in solution for T05L, T10L and T20L samples respectively. Then 10 ml 25% ammonia aqueous solution was added to the suspension and the magnetic sludge was washed using the permanent magnet Nd−Fe−B until pH = 7 and no chloride and sulfate ions. The powders were dried at room temperature. Three different Ti powders were then processed in distilled water at elevated temperature (240°C) and pressure (50 MPa) for 4 h (samples T05L,

T10L and T20L). Sample T05H containing 0.5 g of TiO_2 was processed at 470°C and 42 MPa also for 4 h.

According to experimental data [3], titanomagnetites are formed in very small quantities under these conditions. There is also a significant amount of hematite, indicating strong oxidation of the sample during hydrothermal treatment. The lattice period corresponding to the spinel structure phase is 0.8362−0.8367 nm. This value is intermediate between the lattice constant of maghemite (0.8339 nm) and magnetite (0.8397 nm). Changes in the composition and structure of magnetic particles associated with the diffusion of titanium atoms into the crystalline lattice of magnetite/maghemite or the formation of vacancies and deformations may lead to their chemical heterogeneity.

In Table 1, the basic magnetic characteristics of the samples, obtained experimentally at $T = 295$ K, are given.

According to the magnetic granulometry [5], the ratios of experimental values M_{rs}/M_s and H_{rc}/H_c suggest that the characteristic sizes of ferrimagnetic particles in the samples are close to the single domain or pseudo-single-domain state.

3. Theoretical modeling

For modelled specimens [3,4], the presence of three groups of particles was assumed according to magnetic granulometry, Mössbauer spectroscopy and electronic microscopy data: 1) fraction of chemically heterogeneous two-phase particle composition „magnetite/maghemite — titanomagnetite", 2) weakly magnetic fraction (hematite) and 3) superparamagnetic particles of the first two fractions. Since the average spontaneous magnetization I_{s1} of the first fraction is two orders higher than the weakly magnetic

Table 1. Hysteresis characteristics of the studied samples (M_s — saturation magnetization and M_{rs} — saturation remanence, $\mu_0 H_c$ — coercive force and $\mu_0 H_{cr}$ — remanence coercivity)

1	2	3	4	5	6	7
Sample	M_s, A·m²/kg	M_{rs}, A·m²/kg	M_{rs}/M_s	$\mu_0 H_c$, mT	$\mu_0 H_{cr}$, mT	H_{cr}/H_c
T05L	26.37	2.93	0.11	5.62	14.92	2.66
T10L	19.53	2.07	0.11	4.77	12.61	2.65
T20L	14.11	1.92	0.14	5.97	13.77	2.31
T05H	23.79	4.17	0.18	8.78	18.32	2.09

one (I_{s2}), the two-phase particles should be the primary contribution to the remanence coercivity of M_{rs} samples.

Consider a cubic chemically heterogeneous two-phase particle with an infinitely fine boundary between phases [6–8]. To simplify the estimates, consider that each phase is a homogeneous magnetized crystallographically uniaxial ferrimagnetic composition „magnetite/maghemite" and „titanomagnetite". The inter-phase boundary is parallel to the XZ plane and divides the particle into two parallelepipeds with volumes of $a^3(1 - \varepsilon)$ — phase one and $a^3\varepsilon$ — phase two (a — characteristic particle size, ε — relative phase thickness). As noted earlier, the values of ratios $M_{rs}/M_s = 0.11 - 0.18$ and $H_{cr}/H_c = 2.09 - 2.66$ suggest that single domain and pseudo-single-domain particles [5] prevail in the samples. Therefore, in the simulation, the characteristic size of a ranged from 30 to 80 nm. The thickness of the titanomagnetite phase ε ranged from 0.01 to 0.20, given the increase in the amount of TiO_2 powder dispersed into solution.

The free energy of the two-phase particle, consisting of magneto-crystalline, magnetostatic and Zeeman energies [6], was minimized to obtain magnetic states and magnetization fields. The magnetostatic energy was calculated taking into account the constancy of the surface densities of magnetic charges of mutually parallel and mutually perpendicular rectangles — method of „magnetic rectangles" [6,9,10]. In our case, the two-phase particle in question can be in four states (indices 1 and 2 number the phases): 1) $\theta_1 = 0$, $\theta_2 = 0$; 2) $\theta_1 = \pi$, $\theta_2 = \pi$; 3) $\theta_1 = 0$, $\theta_2 = \pi$; 4) $\theta_1 = \pi$, $\theta_2 = 0$. Here θ_1 and θ_2 — angles between the axis Z and the magnetic moments of the respective phases.

Having determined the magnetization reversal fields of two-phase grains, it is possible to calculate magnetization of an ensemble of identical particles in a given external magnetic field H [11]. In the case of non-interacting particles without an external field, you can determine their relative number in the m-th state

$$n_m|_{H=0} = A \exp(-E_m/(kT)), \qquad (1)$$

where A is found from the normalization condition in which the sum of n_m equals one. Application of an external field parallel to the Z axis does not result in additional states, but only changes their relative shares. Then, assuming a uniform spatial distribution of ferrimagnetic particles in the sample,

the magnetization of the two-phase particle ensemble is equal

$$M(\varepsilon, H) = C_1[I_{sM}(1 - \varepsilon)(n_1 - n_2 + n_3 - n_4)$$
$$+ I_{sT}\varepsilon(n_1 - n_2 - n_3 + n_4)]. \qquad (2)$$

Here $C_1 = Nv/V$ is the volume concentration of the first fraction (N and v are the number and average volume of two-phase particles, V is the sample volume), I_{sM} and I_{sT} are effective spontaneous phase magnetization of phases „magnetite/maghemite" and „titanomagnetite" respectively. The magnetizations of I_{sM} and I_{sT} may have values smaller than I_s of the corresponding minerals, as in addition to chemical heterogeneity, heterogeneity of magnetic moments of phases (appearance of vortices, domain walls etc.) is also possible.

The effect of the random field of the H_i magnetostatic interaction on the magnetic moment of the particle can be accounted for by shifting the magnetization fields to $-H_i$. Suppose that the interaction field H_i has a uniform distribution between $-H_{\max}$ and $+H_{\max}$ [11,12]:

$$H_{\max} \approx 5C_1 I_{s1} \quad \text{at} \quad C_1 < 0.07$$

and

$$H_{\max} \approx 1.3\sqrt{C_1}I_{s1} \quad \text{at} \quad C_1 > 0.07, \qquad (3)$$
$$I_{s1} = I_{sM}(1 - \varepsilon) \pm I_{sT}\varepsilon.$$

Here I_{s1} is the average spontaneous magnetization of two-phase grains. The „+" sign meets the condition of $n_1 = 1$, which corresponds to saturation, i.e., the magnetic moments of both phases are oriented along the applied field (axis Z), and the sign „−" corresponds to a state, when the magnetic moments of the phases are opposite to each other.

It is further assumed that the typical interaction field of the entire $H_{\max}$ system is mainly determined by the two-phase particle group parameters, as the spontaneous magnetization of low-magnetic fraction I_{s2} is two orders lower than I_{s1}. Let's assume that the magnetization reversal of grains occurs simultaneously and independently of each other, which is allowed at a sufficiently large number of particles in the ensemble. Then the calculation of the magnetization of the fraction of two-phase particles with the same ε in the first approximation is reduced to the case

of non-interactive particles with a shift of critical fields to $-H_{\max}$ [11].

The value of the remanence coercivity H_{cr1} for two-phase particles which in our case are in two possible states (n_1 and n_3), is equal to

$$H_{cr1} = H(n_1, n_3) \cdot \left\{1 - [M(n_1) - M(n_1, n_3)]/M(n_1)\right\}$$
$$+ \left\{H(n_1) \cdot [(M(n_1) - M(n_1, n_3))/M(n_1)]\right\}. \quad (4)$$

Here $H(n_1, n_3)$ and $H(n_1)$, $M(n_1, n_3)$ and $M(n_1)$ are the magnetization reversal fields and magnetization of two-phase particles in states n_1 and n_3 or in state $n_1 = 1$, respectively. It should be noted that $M(n_1) = M_{s1}$ is magnetization of the saturation group of two-phase particles. Let's estimate the coercive force of H_{c1} for this group of particles

$$H_{c1} = (H_{cr1} - H_{\max})/3, \quad (5)$$

where the coefficient 1/3 is related to the projection of magnetic moments on the coordinate axes.

In our case, we believe that the light particle axes are chaotic. Therefore, it can be assumed that H_{cr1} corresponds to the average field of magnetization of a single particle, and H_{c1} characterizes the field of magnetization of the entire group of particles. This is due to the fact that when the external field of H is reduced from maximum to 0, there is a redistribution of the magnetic moments of the particles in the directions of the axes and the appearance of magnetic irregularities (vortices, domains, and domain walls). Then the saturation remanent magnetization of M_{rs1} fraction of two-phase ferrimagnetic particles can be estimated as follows:

$$M_{rs1} = \left\{C_1 I_{s1}(M_{rs})/[(C_1 + C_{1sp})I_{s1}(M_s)]\right\}$$
$$\times (H_{c1}/H_{cr1}) \cdot M_{s1}, \quad (6)$$

where C_{1sp} is concentration of superparamagnetic particles of strong magnetic fraction, $I_{s1}(M_{rs})$ and $I_{s1}(M_s)$ are effective spontaneous magnetization in M_{rs} and M_s states, respectively.

Results from X-ray and Mössbauer spectroscopy show the presence of a α-Fe$_2$O$_3$ hematite, which can contribute significantly to the magnetization of the M_s sample, despite low spontaneous magnetization (about several kA/m and even less) [13]. The saturation magnetization of M_{s2} of the low-magnetic fraction is equal to

$$M_{s2} = C_2 \cdot I_{s2}(M_s), \quad (7)$$

where C_2 and $I_{s2}(M_s)$ are volume concentration and spontaneous magnetization (at saturation) of the weakly-magnetic fraction, respectively.

Based on the results of Mössbauer spectroscopy and experimentally obtained relationships of $M_{rs}/M_s = 0.11-0.18$, our samples contain a fairly representative fraction of superparamagnetic particles. In the simulation we will take into account the presence of

two types of superparamagnetic particles belonging to the first (two-phase particles) and second (weakly magnetic) fractions.

The contribution of superparamagnetic particles to saturation magnetization can be estimated using theoretically calculated values of M_{s1} and M_{s2}, and experimentally obtained saturation magnetization value of M_s:

$$M_{ssp} = C_{sp} \cdot I_{ssp}(M_s) = M_s - (M_{s1} + M_{s2}). \quad (8)$$

Here $C_{sp} = C_{1sp} + C_{2sp}$ is the total volume concentration of superparamagnetic particles of strongly and weakly magnetic fractions. The average magnetization of superparamagnetic particles at a saturation of $I_{ssp}(M_s)$ can be estimated by assuming the proportionality of contributions of corresponding fractions with concentrations of C_1 and C_2 to the volume concentrations of the ferrimagnet

$$I_{ssp}(M_s) = I_{s1}(M_s) \cdot [C_1/(C_1 + C_2)]$$
$$+ I_{s2}(M_s) \cdot [C_2/(C_1 + C_2)]. \quad (9)$$

In formula (9), the first term corresponds to the relative contribution of two-phase particles and the second — to the weakly magnetic fraction.

Then, using the experimental values H_{cr} and H_c of the sample, the the values of remanence coercivity H_{cr2} and the coercive force of H_{c2} were estimated

$$H_{cr2} = [H_{cr} - H_{cr1} \cdot C_1/(C_1 + C_2)]/[C_2/(C_1 + C_2)],$$

$$H_{c2} = [H_c - H_{c1} \cdot C_1/(C_1 + C_2)]/[C_2/(C_1 + C_2)]. \quad (10)$$

Superparamagnetic contribution accounting allows estimating the saturation remanence of the weakly-magnetic fraction M_{rs2} similar to formulas (5) and (6), in which H_{c2} and H_{cr2} are consistent with experimental data of (10):

$$M_{rs2} = C_2 I_{s2}(M_{rs})/\left[(C_2 + C_{2sp})I_{s2}(M_s)\right]$$
$$\times (H_{c2}/H_{cr2}) \cdot M_{s2}, \quad (11)$$

where $C_{2sp} = C_{sp} \cdot [C_2/(C_1 + C_2)]$ is concentration of superparamagnetic particles of the weakly magnetic fraction.

Then the total saturation magnetization and saturation remanence are equal

$$M_s = M_{s1} + M_{s2} + M_{ssp}, \quad M_{rs} = M_{rs1} + M_{rs2}. \quad (12)$$

We will assume that the remanence of superparamagnetic particles is approximately zero, as the blocked superparamagnetic particles create a saturation remanence of two orders of magnitude less than M_{rs} of stable particles.

4. Results and discussion

For the strong magnetic phase of the particle composition „magnetite/maghemite — titanomagnetite", given that the phase size is close to the single domain

Table 2. Experimental and theoretically calculated magnetization of samples (M_s — saturation magnetization and M_{rs} — saturation remanence)

1	2	3	4	5
Samples	\multicolumn{2}{c}{$M_s = M_{s1} + M_{s2} + M_{ssp}$, $\text{A} \cdot \text{m}^2/\text{kg}$}		$M_{rs} = M_{rs1} + M_{rs2}$, $\text{A} \cdot \text{m}^2/\text{kg}$
T05L	26.37	$10.07 + 0.26 + 16.04$	2.93	$2.86 + 0.07$
T10L	19.53	$7.26 + 0.24 + 12.03$	2.07	$2.02 + 0.05$
T20L	14.11	$6.20 + 0.30 + 7.61$	1.92	$1.84 + 0.08$
T05H	23.79	$22.14 + 0.60 + 1.05$	4.15	$3.79 + 0.36$

size, and ignoring possible irregularities of the magnetic moment, assume that spontaneous magnetization is $I_{s11}(M_{rs}) = I_{s11}(M_s) = 400\,\text{kA/m}$. For the less magnetic phase (titanomagnetite) spontaneous magnetization $I_{s12}(M_{rs}) = I_{s12}(M_s) = 380\,\text{kA/m}$.

Since the saturation remanence Mrs is known for each sample, which is mainly provided by the two-phase particle ensemble, the most appropriate volume concentration of the strong magnetic fraction C_1 was obtained in the range of $0.03-0.11$. The best agreement with experimental data for samples T05L, T10L and T20L synthesized at $240°C$ was obtained for concentrations of strong magnetic, weakly magnetic and superparamagnetic fractions, respectively, in the following ranges: $C_1 = 0.03-0.05$, $C_2 = 0.16-0.20$ and $C_{sp} = 0.27-0.34$.. For a T05H sample processed at $470°C$, the best concentration is $C_1 = 0.11$, $C_2 = 0.40$ and $C_{sp} = 0.02$. The low concentration of superparamagnetic particles in this sample is likely due to synthesis conditions leading to the formation of larger particles on average. The theoretical total ferrimagnet concentration in all samples is in the range of $0.50-0.56$. In Table 2 the comparison of experimental and theoretically calculated values of magnetization is given.

Experimental values of M_s and M_{rs} are presented in columns 2 and 4. Columns 3 and 5 contain the total values of theoretically calculated saturation magnetization (M_{s1}, M_{s2}, M_{ssp}), and saturation remanence (M_{rs1}, M_{rs2}) of the corresponding three fractions. Theoretical values of H_c and H_{cr} of samples are equal to experimental values according to formulas (4), (5) and (10).

5. Conclusion

The application of the model of an ensemble of chemically heterogeneous magnetostatic interacting particles allowed to theoretically calculate hysteresis characteristics of composites $Fe_3O_4-Fe_{3-x}Ti_xO_4$.

The separation of three fractions of ferrimagnetic particles — two-phase strong magnetic (magnetite/maghemite — titanomagnetite), weakly magnetic (hematite) and superparamagnetic particles — made it possible to simplify calculations and verify the model used. It is shown that

the main contribution to remanence is made by chemically heterogeneous particles, and superparamagnetic particles make a significant contribution to saturation magnetization for samples obtained at $240°C$. For a sample obtained at $470°C$, the fraction of superparamagnetic particles is small due to the synthesis conditions leading to the formation of larger particles.

In the assumption of the uniform spatial distribution of ferrimagnetic particles in the sample and the uniform distribution of the random field of magnetostatic interaction, a theoretical evaluation of the values of the mean (effective) spontaneous magnetization, the mean values of remanence coercivity and coercive force of the respective fractions and the whole ensemble, which are well consistent with experimental data for all samples, was made.

Conflict of interest

The authors declare that they have no conflict of interest.

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