Conference materials
UDC 537.622, 537.624
DOI: https://doi.org/10.18721/JPM.153.127

Micromagnetic modeling of the superparamagnetic fraction of Fe_3O_4–$Fe_{3-x}Ti_xO_4$ composites

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Abstract: Modeling of the hysteresis characteristics of Fe_3O_4–$Fe_{3-x}Ti_xO_4$ composites was performed using the method of magnetic rectangles. Their magnetic properties are well explained within the model of an ensemble of magnetostatically interacting two-phase chemically inhomogeneous particles. It is shown that accounting for the contribution of the superparamagnetic fraction makes it possible to obtain agreement between the theoretical and experimental magnetic characteristics of the samples. The model allows calculating the magnetization reversal fields and magnetizations of the studied composites theoretically and also to show that the main contribution to the remanent magnetization is made by two-phase particles. In addition, a possibility of using this model for samples containing superparamagnetic particles is demonstrated.

Keywords: magnetic granulometry, superparamagnetism, micromagnetic modeling, magnetostatic interaction, two-phase particles

Citation: Ralin A. Yu., Kharitonskii P. V., Zolotov N. A., Gareev K. G., Anikieva Yu. A., Micromagnetic modeling of the superparamagnetic fraction of composites Fe_3O_4–$Fe_{3-x}Ti_xO_4$, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 15 (3.1) (2022) 162–167. DOI: https://doi.org/10.18721/JPM.153.127

Материалы конференции
УДК 537.622, 537.624
DOI: https://doi.org/10.18721/JPM.153.127

Микромагнитное моделирование суперпарамагнитной фракции в композитах Fe_3O_4–$Fe_{3-x}Ti_xO_4$

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Аннотация. Методом «магнитных прямоугольников» проведено моделирование гистерезисных характеристик композитов Fe_3O_4–$Fe_{3-x}Ti_xO_4$. Их магнитные свойства хорошо объясняются в рамках модели ансамбля магнитостатически взаимодействующих двухфазных химически неоднородных частиц. Данная модель позволила теоретически рассчитать поля перемагничивания и намагниченности исследуемых композитов, а также показать, что основной вклад в остаточную намагниченность вносят двухфазные частицы. Используемая модель применима для образцов, содержащих суперпарамагнитные частицы.

Ключевые слова: магнитная гранулометрия, суперпарамагнетизм, микромагнитное моделирование, магнитостатическое взаимодействие, двухфазные частицы

Ссылка при цитировании: Ралин А. Ю., Харитонский П. В., Золотов Н. А., Гареев К. Г., Аникиева Ю. А. Микромагнитное моделирование суперпарамагнитной фракции в композитах Fe_3O_4–$Fe_{3-x}Ti_xO_4$ // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.1. С. 162–167. DOI: https://doi.org/10.18721/JPM.153.127

Introduction

Theoretical works dedicated to ensembles of superparamagnetic (SP) particles often use the approximation of non-interacting particles, assuming their chemical homogeneity. Earlier studies [1, 2] considered Fe_3O_4–$Fe_{3-x}Ti_xO_4$ composites, where the presence of a significant fraction of SP particles was found. It was shown that the magnetic properties of the studied samples cannot be explained without accounting for the chemical inhomogeneity of individual particles and the magnetostatic interaction between them, including the SP fraction. Existing micromagnetic modeling methods allow to investigate in detail the magnetic states of individual grains (e.g., [3, 4]). However, significant computational resources are required for considering even small sets of such grains. The approach we adopt allows making a simpler estimate of the magnetic states of individual particles and their ensembles [5, 6].

Materials and Experimental data

Synthesis of composites based on the Fe_mO_n–TiO_2 system was carried out by magnetite precipitation in suspension of TiO_2 powder [1, 2]; 4 g of $FeCl_3{\cdot}6H_2O$ and 2 g of $FeSO_4{\cdot}7H_2O$ (molar ratio 2:1) were dissolved in 100 mL of distilled water. Samples T05L, T10L, and T20L were obtained by dispersing TiO_2 powder (0.5, 1.0, and 2.0 g, respectively) into solution, followed by hydrothermal treatment (240 °C, 50 MPa) for 4 hours. Sample T05H was treated under different conditions (470 °C, 42 MPa). Sample T20R was not subjected to temperature treatment.

According to the experimental data [1, 2], titanomagnetites are formed in very small quantities under the specified conditions. Significant content of hematite is detected, indicating significant oxidation of the samples during processing. The lattice period of 0.8362–0.8367 nm is intermediate between the constants of the lattice of maghemite and magnetite.

Since the particles are grouped into conglomerates, embedding of titanium atoms into the ferrimagnetic does not occur on all sides, but only from a limited number of surfaces. For simplicity, we will assume that titanomagnetite is formed only on one side of the ferrimagnetic particle, i.e., chemically heterogeneous two-phase particles are formed. Since there is little titanomagnetite, the corresponding phase is a thin layer. Besides, if the particle size is smaller than the single-domain size, then two-phase particles that are in a SP state should be present.

Table 1 shows the characteristics of the samples [1, 2]: M_s is the saturation magnetization and M_{rs} is the saturation remanence, H_c is the coercive force and H_{cr} is the remanence coercivity.

For the first four samples, the ratios of M_{rs}/M_s values are in the range of 0.1–0.2 and H_{cr}/H_c in the range of 2–3. For sample T20R, these ratios are approximately 0.01 and 4, respectively. According to magnetic granulometry data, it can be assumed that the first group of samples is dominated by single- and low-domain particles, whereas in sample T20R by SP particles.

Theoretical Modeling

For the modeled samples [1, 2], the presence of three groups of particles was assumed: 1) a fraction of chemically inhomogeneous two-phase particles (magnetite/maghemite–titanomagnetite), 2) a weakly magnetic fraction (mainly hematite), and 3) superparamagnetic particles of the first two fractions. Since the spontaneous magnetization I_{s1} of the first fraction is two orders of magnitude higher than that of the weakly magnetic fraction (I_{s2}), the two-phase particles make the main contribution to the saturation remanent magnetization of M_{rs} samples.

Table 1

Hysteresis characteristics of the samples

Sample	M_s, A·m²/kg	M_{rs}, A·m²/kg	$\mu_0 H_c$, mT	$\mu_0 H_{cr}$, mT	M_{rs}/M_s	H_{cr}/H_c
T05L	26.37	2.95	5.62	14.92	0.11	2.66
T10L	19.53	2.06	4.77	12.61	0.11	2.65
T20L	14.11	1.92	5.97	13.77	0.14	2.31
T05H	23.79	4.15	8.78	18.32	0.18	2.09
T20R	28.95	0.35	0.51	1.90	0.01	3.73

The first fraction is an ensemble of cubic two-phase particles with an infinitely thin boundary between the phases [5]. Each phase is a homogeneously magnetized crystallographically uniaxial ferrimagnetic (magnetite/maghemite and titanomagnetite). The characteristic size of particle a ranged from 20 to 80 nm, and the relative thickness of the second phase $\varepsilon = 0.05$–0.20.

To find the magnetic states and critical fields of remagnetization, the free energy was minimized, including magnetocrystalline, magnetostatic, and Zeeman energies. The magnetostatic energy was calculated by the method of magnetic rectangles [5, 6]. In this case, the two-phase particle can be in four states: the magnetic moments of the phases are parallel to each other along (n_1) or against (n_2) the external magnetic field H or antiparallel to each other (n_3 and n_4). In the absence of an external field, it is possible to determine their relative number in the mth state:

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

where A is found from the normalization condition, in which the sum of n_m equals unity.

Then the magnetization of the ensemble of two-phase ferrimagnetic particles is [5]:

$$M\left(\varepsilon, H\right) = C_1 \left[I_{s\,sm}\left(1-\varepsilon\right)\left(n_1 - n_2 + n_3 - n_4\right) + I_{s\,wm}\varepsilon\left(n_1 - n_2 - n_3 + n_4\right)\right]. \tag{2}$$

Here $C_1 = N \cdot v / V$ 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), and $I_{s\,sm}$ and $I_{s\,wm}$ are the effective spontaneous magnetizations of the first and second phases, respectively.

If we assume that the random fields of magnetostatic interaction H_i are uniformly distributed in the interval from $-H_{max}$ to $+H_{max}$, 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-interacting particles with a shift of the critical fields by $-H_{max}$ [5]:

$$\begin{gathered} H_{max} \approx 5 C_1 I_{s1} \text{ at } C_1 < 0.07 \text{ and } H_{max} \approx 1.3\sqrt{C_1} I_{s1} \text{ at } C_1 > 0.07\ , \\ I_{s1} = I_{s\,sm}\left(1-\varepsilon\right) \pm I_{s\,wm}\varepsilon\ ,\ K_{u1} = K_{u\,sm}\left(1-\varepsilon\right) + K_{u\,wm}\varepsilon\ . \end{gathered} \tag{3}$$

Here I_{s1} is the average spontaneous magnetization of a two-phase grain. The plus sign corresponds to the state $n_1 = 1$ (saturation) when the magnetic moments of both phases are oriented along the applied field, and the minus sign indicates the state when the magnetic moments of the phases are directed opposite to each other. $K_{u\,sm}$ and $K_{u\,wm}$ are the crystallographic anisotropy constants of the strongly magnetic (magnetite) and less magnetic (titanomagnetite) phases, respectively, and K_{u1} is the average constant of a two-phase grain (magnetite – $I_s = 484$ kA/m, $K_u = 1.36 \cdot 10^4$ J/m^3; titanomagnetite ($x = 0.1$) – $I_s = 426$ kA/m, $K_u = 2.5 \cdot 10^4$ J/m^3; $T = 290$ K [7]).

During modeling, the saturation remanence was provided by the strongly magnetic two-phase particles and the weakly magnetic fraction. However, it was possible to agree the theoretical values of the saturation magnetization with the experimental data only in the assumption of the presence of a large number of SP particles in the samples. Then for the first four samples

$$M_s = M_{s1} + M_{s2} + M_{s\,sp}, \;\; M_{rs} = M_{rs1} + M_{rs2}. \tag{4}$$

where M_{s1} and M_{rs1}, M_{s2} and M_{rs2}, $M_{s\,sp}$ are the magnetizations of the corresponding three fractions.

Judging by the hysteresis characteristics (Table 1), the fifth sample (T20R) contains mainly superparamagnetic particles. Therefore, the average particle size of this sample varied in the range of 20–30 nm (for spherical magnetite grains, the single-domain size is 29–36 nm). The contribution of all particles to the saturation magnetization was taken into consideration, and only the particles blocked due to the magnetostatic interaction were included in the remanence. In this case, the two-phase particle model was also used for the strongly magnetic fraction.

Magnetostatic interaction results in that a particle with the volume $v > v_b(H_i)$ can contribute to the remanence. Here $v_b(H_i)$ is the volume of a particle whose magnetic moment remains stable when the particle is exposed to the interaction field H_i [8]. In this case, the blocking volume is

$$v_b\left(H_i\right) = \begin{cases} v_b / \left(1 + \left|H + H_i\right| / H_0\right)^2, & \left|H + H_i\right| \le H_0; \\ v_b / \left(4\left|H + H_i\right| / H_0\right), & \left|H + H_i\right| > H_0. \end{cases} \tag{5}$$

Here $H_0 \approx H_{cr}$ is the magnetization reversal field, and $v_b \approx 50kT/(I_s H_0)$ is the blocking volume in the zero field [9]. For interacting SP particles, the time-averaged magnetic moment is [8]:

$$m = vI_s \tanh\left[v_b\left(H_i\right) I_s \left|H + H_i\right| / kT\right] = vI_{s\,sp}, \tag{6}$$

where $I_{s\,sp}$ is the effective spontaneous magnetization of two-phase SP particles blocked due to magnetostatic interaction, which coincides with $I_s = I_{s1}$ in the saturation field, and when calculating the saturation remanence is about a tenth of the value. Then for the SP sample T20R

$$M_s = M_{s1\,b} + M_{s2\,b} + M_{s\,nb}, \;\; M_{rs} = M_{rs1\,b} + M_{rs2\,b}, \tag{7}$$

where $M_{s1\,b}$ and $M_{rs1\,b}$, $M_{s2\,b}$ and $M_{rs2\,b}$ correspond to the blocked particles and $M_{s\,nb}$ to the unblocked particles. The magnetization reversal fields of the SP particles blocked by the interaction can be estimated as [10]:

$$H_{0\,sp} = H_{0\,sd}\left\{1 - \left[v_b\left(H_i\right)/v\right]^{1/2}\right\}, \tag{8}$$

where $H_{0\,sd}$ is the magnetization reversal field of a single-domain particle, and the value of v lies in the range from v_b (without regard to the interaction) to the critical volume of the single-domain. Since most of the particles in the sample T20R are superparamagnetic, then $v \approx v_b$.

Results and Discussion

After calculating the fields H_0 of the strongly magnetic fraction using the uniaxial two-phase particle model and provided that $H_0 = H_{cr1}$, we estimated the coercive force of this group of particles H_{c1}. The value of the coercive force in terms of remanent magnetization for two-phase particles, which in our case are in two possible states n_1 and n_3, is equal to:

$$H_{cr1} = H\left(n_1, n_3\right)\cdot(1 - \Delta) + H\left(n_1\right)\cdot\Delta, \;\; \Delta = \left[M\left(n_1\right) - M\left(n_1, n_3\right)\right] / M\left(n_1\right). \tag{9}$$

Here $H(n_1,n_3)$ and $H(n_1)$, $M(n_1, n_3)$ and $M(n_1)$ are the reversal fields and magnetizations of two-phase particles (Eq. (2)) in the states n_1 and n_3 and in the state $n_1 = 1$, respectively. It should be noted that $M(n_1) = M_{s1}$. Let us estimate the coercive force of this fraction of particles as $H_{c1} = (H_{cr1} - H_{max})/3$, where the factor 1/3 accounts for the disordering of magnetic moments' orientations when the external field is removed.

Further on, using the experimental values of H_c and H_{cr} of the sample, we estimate the values of the coercive force and the remanence coercivity for the weakly magnetic fraction with the volume concentration C_2 ($\delta_1 = C_1/(C_1 + C_2)$ and $\delta_2 = C_2/(C_1 + C_2)$ are the relative concentrations):

$$H_{c2} = \left(H_c - H_{c1} \cdot \delta_1\right) / \delta_2, \; H_{cr2} = \left(H_{cr} - H_{cr1} \cdot \delta_1\right) / \delta_2. \tag{10}$$

Saturation remanence of the fraction of two-phase ferrimagnetic particles (i = 1) and weakly magnetic fraction (i = 2) can be written as follows [11]:

$$M_{rsi} = \frac{C_i I_{rsi}}{(C_i + C_{i\,sp}) I_{si}} \cdot \frac{H_{ci}}{H_{cri}} \cdot M_{si}, \tag{11}$$

where $C_{i\,sp}$ is the concentration of SP particles, I_{rsi} and I_{si} are the effective magnetizations in M_{rs} and M_s states, respectively, and their ratio characterizes the decrease of remanence due to chemical and magnetic inhomogeneities (see Eq. (3)). For the SP sample T20R, the same model of interacting uniaxial two-phase particles was used, taking into consideration Eqs. (6-8).

Table 2 shows the calculated magnetizations for the studied samples. The best agreement with the experiment was obtained with the following parameters. For the first four samples: a = 60 nm (greater than the single-domain size of magnetite), ε = 0.05–0.20 (according to the amount of TiO_2 added during synthesis 0.5–2.0 g), $I_{s\,sm}$ = 400 kA/m and $I_{s\,wm}$ = 380 kA/m, I_{s2} = 3 kA/m (corresponding to hematite). For the SP sample T20R: a = 30 nm (close to the single-domain size), ε = 0.05, $I_{s\,sm}$ = 15 kA/m and $I_{s\,wm}$ = 13 kA/m (see Eqs. (3) and (6)), I_{s2} = 3 kA/m.

Table 2

Theoretical values of magnetizations, A·m²/kg

Sample	$M_s = M_{s1} + M_{s2} + M_{s\,sp}$		$M_{rs} = M_{rs1} + M_{rs2}$	
T05L	26.37	10.07 + 0.26 + 16.04	2.95	2.89 + 0.06
T10L	19.53	7.26 + 0.24 + 12.03	2.06	2.02 + 0.04
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
	$M_s = M_{s1\,b} + M_{s2\,b} + M_{s\,nb}$		$M_{rs} = M_{rs1\,b} + M_{rs2\,b}$	
T20R	28.95	23.74 + 0.51 + 4.70	0.35	0.23 + 0.12

As can be seen from the table, the calculated total values of M_s and M_{rs} of the samples (Table 1) coincide with the experimental values. In all the samples except for the sample T05H obtained at a higher temperature, a large fraction of SP particles is present. In the sample T20R, SP particles clearly dominate, with a significant portion of them blocked due to magnetostatic interaction.

For the first three samples, the theoretical values of the ferrimagnetic volume concentrations of the fractions under consideration are in the following ranges: C_1 = 0.03–0.05, C_2 = 0.16–0.20, C_{sp} = 0.27–0.34. For the sample T05H: C_1 = 0.11, C_2 = 0.40, C_{sp} = 0.02; such values are apparently connected with enlargement of particles and oxidation of magnetite into hematite upon heating. For the SP sample T20R: C_1 = 0.12, C_2 = 0.34, C_{sp} = 0.09; here C_1 and C_2 correspond to the blocked particles of the first two fractions, C_{sp} to the unblocked ones. The second fraction makes a relatively significant contribution to M_{rs} only in the case of the samples T05H and T20R.

Conclusion

The hysteresis characteristics of the simulated composites are well explained within the model of an ensemble of magnetostatically interacting two-phase particles. The superparamagnetic fraction largely determines the magnetic properties of the samples, and its consideration makes it possible to agree their theoretical and experimental characteristics.

Isolation of three fractions of ferrimagnetic particles: strongly magnetic chemically inhomogeneous particles (magnetite/maghemite–titanomagnetite), weakly magnetic particles (hematite, goethite, and other iron hydroxides) and superparamagnetic particles belonging to the first two fractions, served as a basis for theoretical modeling. Assuming a uniform spatial distribution of ferrimagnetic particles, we used a random magnetostatic interaction field approximation and obtained theoretical estimates of average (effective) spontaneous magnetizations I_{s1} and I_{s2}, remanence coercivities H_{cr1} and H_{cr2}, and coercive forces H_{c1} and H_{c2} of the corresponding particle fractions, which are in good agreement with the experimental data.

The model of two-phase interacting particles allows calculating the magnetization reversal fields and magnetizations of the studied composites theoretically and to show that the main contribution to the remanence is made by chemically inhomogeneous particles. The possibility of using this model for samples containing superparamagnetic particles is demonstrated.

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Received 14.05.2022. Approved after reviewing 13.06.2022. Accepted 13.06.2022.