MICROMAGNETIC MODELING OF THE SUPERPARAMAGNETIC FRACTION OF COMPOSITES Fe_3O_4–$Fe_{3-x}Ti_xO_4$

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Theoretical works devoted to the study of ensembles of superparamagnetic (SP) particles often use the «non-interacting particles» approximation and the assumption of their chemical homogeneity. The authors [1,2] studied composites, in which 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 taking into consideration the chemical inhomogeneity of individual particles and the magnetostatic interaction between them.

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]. 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 470 °C and 42 MPa. Sample T20R was not subjected to temperature treatment.

Table 1 shows the characteristics of the samples: M_s is the saturation magnetization and M_{rs} is the saturation remanence, $\mu_0 H_c$ is the coercive force and $\mu_0 H_{cr}$ is the remanence coercivity. According to magnetic granulometry [3], it can be assumed that the first group of samples is dominated by single- and low-domain particles, whereas in T20R by SP particles.

Table 1. Hysteresis characteristics of the samples [1,2]

Sample	M_s, A·m^2/kg	M_{rs}, A·m^2/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

For the modeled samples, the presence of three groups of particles was assumed: 1) the fraction of chemically inhomogeneous two-phase particles (magnetite/maghemite – titanomagnetite), 2) the 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.

The first fraction is an ensemble of cubic two-phase particles with an infinitely thin boundary between the phases [4]. 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 ε ranged from 0.05 to 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 considering the constancy of surface magnetic charge densities of mutually parallel and mutually perpendicular rectangles – the "magnetic rectangles" method [4, 5]. In this case, the two-phase particle can be in four states: the magnetic moments of the phases are parallel to each other (along or against the external magnetic field H) or antiparallel to each other (Fig. 1).

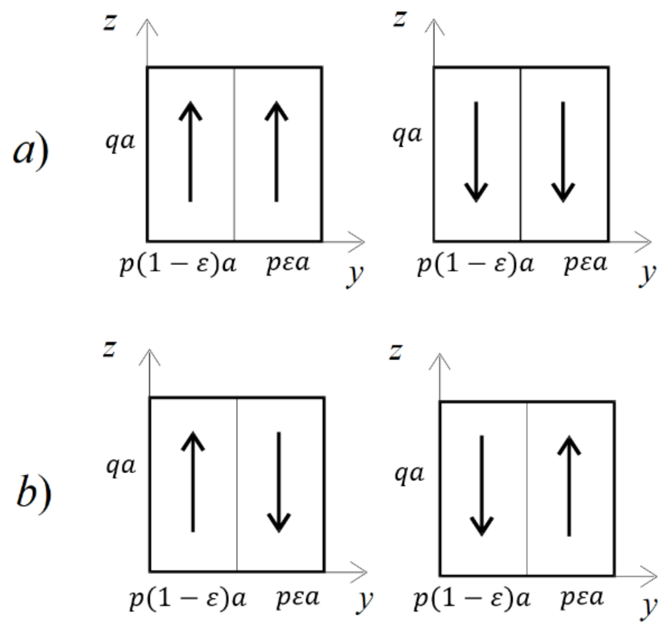

Fig. 1. Possible states of a two-phase particle.

In the case of non-interacting particles in the absence of an external field, it is possible to determine their relative number in the m-th state:

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

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

Then the magnetization of the ensemble of two-phase ferrimagnetic particles is [4]:

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

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 $-H_{max}$ [4].

During modeling, the saturation remanent magnetization in the first approximation 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 superparamagnetic particles in the samples.

Then for the first four samples

$$M_s = M_{s1} + M_{s2} + M_{s\,sp}, \quad M_{rs} = M_{rs1} + M_{rs2}, \tag{3}$$

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 [6]). 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 remanent magnetization. Here $v_b(H_i)$ is the critical volume of a particle whose magnetic moment remains stable when the particle is exposed to the interaction field H_i [7]. For superparamagnetic interacting particles, the time-averaged nonzero magnetic moment contributing to the remanent magnetization is [7]:

$$m = vI_s \tanh[v_b(H_i)I_s|H + H_i|/kT] = vI_{s\,sp}, \tag{4}$$

where $I_{s\,sp}$ is the effective spontaneous magnetization of two-phase superparamagnetic particles blocked due to magnetostatic interaction, which coincides with $I_s = I_{s1}$, in the saturation field, while the calculation of the saturation remanent magnetization is tens of times smaller.

Then for the superparamagnetic sample T20R

$$M_s = M_{s1\,b} + M_{s2\,b} + M_{s\,nb}, \quad M_{rs} = M_{rs1\,b} + M_{rs2\,b}, \tag{5}$$

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.

Having calculated the critical fields of remagnetization H_0 of the strongly magnetic fraction using the two-phase particle model and assuming that $H_0 = H_{cr1}$, we estimated the coercive force of this group of particles H_{c1}. Then, using the experimental values (Table 1), we fitted H_{cr2} and H_{c2}. Taking into consideration the shares of the fractions, the average theoretical values of H_c and H_{cr} of the samples coincided with the experimental ones.

Table 2 shows the calculated magnetization values, which in total are equal to the experimental M_s and M_{rs} of the samples.

Table 2. Theoretical values of magnetizations, A·m^2/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

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.

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