Magnetic Properties of the Ultrafine Co Particle Systems

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The method for evaluation of the particle size distribution of fine particles from hysteresis loop measurements is presented. The method is illustrated on the SiO$_2$-based Co nanoparticle systems. The influence of technological conditions of sample preparation onto particle size distribution is investigated.

Key words : nanoparticle, superparamagnetism, exchange length, particle distribution

1. Introduction

During last two decades studying the magnetic ultrafine particle systems becomes more and more active because of continuous broadening of the area of application of new magnetic materials. Magnetic properties of these systems strongly differ from properties of bulk materials made from the same constituents. At reduction of the grain size the ratio of a surface area of particle to its total volume grows up. While crushing of a ferromagnetic multidomain material to finer particles, qualitative jump in physical properties occurs when the majority of particles achieve a single domain limit. According to Ref. 1, the largest size of single domain Fe- and Ni-particles does not exceed 20 and 60 nm, respectively. On the other hand, the formation of oxides and other chemical compounds on the grain surface also affects on the physical properties of the fine particle systems, for example, it can result to appearance of the uniaxial anisotropy [2]. The further crushing of particles leads in transition to a superparamagnetic state. For the majority of ferromagnetic materials a transition from ferromagnetic to superparamagnetic state is possible when the grain size does not exceed 1-10 nm [3]. In this state behavior of a system is determined by the thermal fluctuations of magnetic moments of particles. When number of atoms in particles reaches hundreds or tens, quantum dimensional effects start to play an important role. Another point is, that a presence of the neighboring particles strongly influences the behavior of the particle in

magnetic field. Therefore, many theories of particles interactions exist up to date [4].

Up to now many experimental techniques for the preparation and investigation of fine particles materials are known (see, for example, review [5] and references therein). While modeling the system with given properties it is helpful to know the exact data on morphology and size distribution of grains. In the given study we present a method for determining the particles size distribution on a basis of the magnetic measurements data.

2. Sample preparation

Co/SiO$_2$ samples consisting fine Co particles were produced at the Chemistry Department of Moscow State University (the group leader is Dr. P. Chernavskii). Porous material (silica gel) with surface density 80 m^2/g and porous size about 5 nm was filled by the solution of Co nitrate Co(NO$_3$)$_2$*6H$_2$O of the given concentration. After impregnation the samples were dried in the air atmosphere at 120°C within 4 hours, and then were annealed at 500°C within 6 hours. Thus, the Co$_3$O$_4$/SiO$_2$ systems with 10 at.% Co were obtained. Then samples were reduced in a hydrogen atmosphere. The cell of vibrating magnetometer was used as a reactor that allowed to control the magnetization of a sample. Magnetization was assumed to be proportional to the weight of metal Co. Thus, investigations of magnetic properties were carried out on samples further designated as r5, r13, r14, r22, r30, r62 where symbol 'r' means reduction, and the following number designates a degree of reduction; e.g., the abbreviation r13 means that the mass fraction of metal cobalt is 13%

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and the mass fraction of cobalt oxides is 87%.

Also a series of samples r100ox51, r100ox56, r100ox71, r100ox89, r50ox20 was studied. In this case 'ox' means oxidation and a following number designates a degree of oxidation, e.g., in the sample r100ox56 cobalt oxides were reduced up to 100% and then metal cobalt was oxidized on 56%. Oxidation was performed in the 1%O_2 +99%He atmosphere. For the given series of samples reduction was carried out at 500°C.

The attempt was also undertaken to receive the fine particles having significantly different sizes. For this purpose the samples 73H300 and 73HO300 were prepared by reduction in the hydrogen atmosphere at 300°C and in the mixture of water vapor and hydrogen, respectively. Next samples 73ar500, 73hr500 were reduced at 500°C in 5%H_2+95%Ar atmosphere and in the pure hydrogen, respectively. The idea of such scheme of preparation was based on the assumption that an addition of argon or water vapor to hydrogen would increase the relative growth rate of ferromagnetic single domain particles with respect to growth rate of superparamagnetic particles, and, therefore, the oxidation of superparamagnetic particles would performed in parallel to the reduction process. Therefore, a dynamical balance of number of superparamagetic particles could occur.

We have also carried out the investigations of a series of samples 73ar350, 73ar400, 73ar450, 73ar480, 73ar500. In this case 73 means number of a technological cycle (at all previous series specified above this cycle was the same), 'ar' means, that reduction was performed in the mixture 5%H_2+95%Ar at temperatures 350, 400, 450, 480 and 500°C, respectively.

3. Evaluation of the particle size distribution from hysteresis loops

The purpose of present research was to find a simple way to evaluate the particle size distribution from magnetic measurements data, namely, from measurement of hysteresis loops that requires the simplest set-up and can be conducted in any laboratory. We have measured the hystereris loops using vibrating sample anisometer. The experimental set-up was described earlier [6]. The analysis of experimental hysteresis loops (typical example is shown in Fig. 1) for the prepared samples containing fine Co particles (namely, a presence of residual magnetization, nonsaturation of loops in large, about 8000 Oe, magnetic fields), allows us to conclude, that nanoparticles can be divided into two groups. The first group (or fraction) consists of "small" superparamagnetic particles which behavior in magnetic field is described by Langeven
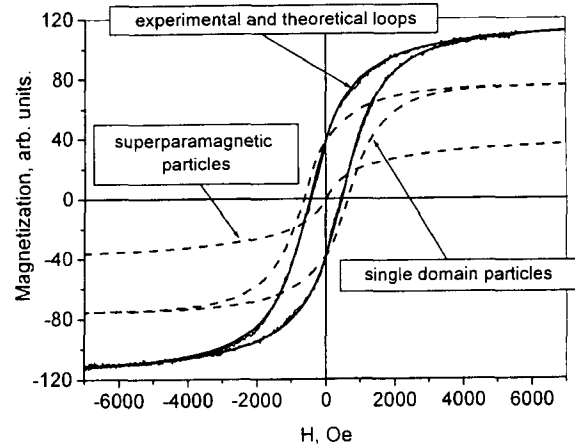

Fig. 1. Typical experimental and calculated hysteresis loops for fine Co particle system (sample r14), illustrating the theoretical approach presented in the text.

function averaged over particle size distribution [7]. The second group of particles ("large" particles) consists of granules of the larger size having anisotropy, magnetization behavior of which has a hysteresis in magnetic field. For calculation of the particle size distribution we will suppose, that all particles are single domain, have the spherical form, and we assume that the large particles have the uniaxial anisotropy.

We will describe small and large particles by log-normal distribution [8, 9, 10]

$$f(d)=A_0 \exp\left\{ -\frac{\ln^2(d/d_m)}{2\ln^2\sigma} \right\}, \tag{1}$$

here d is a diameter of the particle, A_0 is a normalizing factor, d_m and σ represent statistical median and geometric standard deviation. Considering as a first approximation, that two fractions of particles are independent subsystems, we can present the full particle size distribution as a sum of two log-normal distributions

$$P(d)=\alpha f_1(d)+\beta\ f_2(d) \tag{2}$$

with weights α and β, where $f_1(d)$ describes superparamagnetic particles, and $f_2(d)$ describes single domain particles, having the anisotropy.

Neglecting the anisotropy energy for small superparamagnetic particles, we can simply write down the contribution to the hysteresis loop from the first fraction of particles as the Langeven function averaged over distribution $f_1(d)$:

$$M=\sum_{i=1}^{N} \left\{ M_{Co}\frac{4\pi}{3}\left(\frac{d_i}{2}\right)^3 f_1(d_i)L(\alpha_i) \right\}, \tag{3}$$

$$L(\alpha)=\coth \alpha - 1/\alpha,$$

and

$$\alpha_i=\frac{M_{Co}H4\pi}{k_BT}\frac{}{3}\left(\frac{d_i}{2}\right)^3,$$

where M_{Co} is a magnetic moment of Co per unit volume, k_B is Boltzmann constant, and T is temperature.

We will describe the second fraction (large particles) by the well-known Stoner and Wohlfarth model [11] for non-interacting single domain particles with uniaxial magneto-crystalline anisotropy and easy axis oriented randomly in space. Thus, for particles having fixed size we get the initial hysteresis loop [11, 12] with coercivity $H_C \approx K_u/M_s$, (here K_u is effective anisotropy constant and M_s is saturation magnetization) and with residual magnetization being equal to $0.5M_s$.

For calculation of the contribution to the hysteresis loop coming from the second fraction of particles one has to average the initial hysteresis loop over size distribution $f_2(d)$, taking into account the dependence of coercivity H_C on the grain size d. If the grain size is less, than the ferromagnetic exchange length,

$$L_{ex}^0=\sqrt{A/K_1} \qquad (4)$$

(here A is exchange stiffness constant, K_1 is anisotropy constant), then the ferromagnetic exchange tends to align the moments of the neighboring grains parallel to each other. This effect is described by so-called random aniso-tropy model [13, 14]. Magnetization of each granule in this case does not follow simply to the direction of the easy axis. The effective anisotropy is an average over several grains in the nearest environment and, consequently, is reduced in magnitude. According to the theory [14], the effective anisotropy constant responsible for magnetization process, is determined as:

$$K_u \approx K_1(d/L_{ex}^0)^6=K_1^4d^6/A^3 . \qquad (5)$$

Hence, coercivity for a grain of diameter d reads as

$$H_c \approx \frac{K_1}{I_s}\left(\frac{d}{L_{ex}^0}\right)^6 \qquad (6)$$

Taking into account, that log-normal distribution (1) depends only on a dimensionless combination (d/d_2) where d_2 is statistical median of distribution $f_2(d)$, we will describe ensemble of large particles using two parameters: a dispersion σ_2 and coercivity

$$H_c^0=\frac{K_1}{I_s}\left(\frac{d_2}{L_{ex}^0}\right)^6 . \qquad (7)$$

Knowing, that for the initial hysteresis loop [11, 12] the residual magnetization is equal to 1/2 of saturation magnetization, we find from experimental loop the saturation magnetization for the second group of particles, as $2M(0)$, where $M(0)$ is the residual magnetization. The ensemble of superparamagnetic particles is described by two parameters of log-normal distribution $f_1(d)$: a maximum of distribution function d_1 and a dispersion σ_1.

Four parameters being included in our model, d_1, σ_1, H_c^0, σ_2, are determined using numerical procedure of minimization of a root-mean-square deviation between a theoretical and experimental loop. A magnitude of the saturation magnetization for superparamagnetic particles can be determined at each step of the minimization procedure from experimental loop.

From (7) one can find a maximum of distribution function d_2 for the large particles:

$$d_2=L_{ex}^0(H_c^0/H_0)^{1/6} , \qquad (8)$$

where

$$H_0 \approx \frac{K_1}{I_s} \qquad (9)$$

is the coercivity of the initial loop [11, 12].

Weights α and b of the distribution $P(d)$ (Eq. 2) can be found using a normalization condition and the condition of proportionality of volumes of two fractions of particles to their saturation magnetizations $M_s^{(1)}$ и $M_s^{(2)}$:

$$\alpha+\beta=1, \quad \frac{\alpha V_1}{\beta V_2}=\frac{M_s^{(1)}}{M_s^{(2)}} \qquad (10)$$

where

$$V_1=\sum_{i=1}^N \left\{\frac{4\pi}{3}\left(\frac{d_i}{2}\right)^3 f_1(d_i)\right\},$$
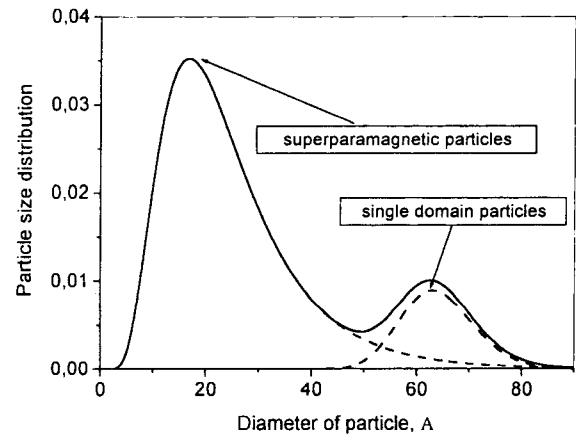

Fig. 2. Particle size distribution of fine Co particles (sample r14) evaluated from hysteresis loop shown in Fig. 1.

$$V_2 = \sum_{i=1}^{N} \left\{ \frac{4\pi}{3}\left(\frac{d_i}{2}\right)^3 f_2(d_i) \right\} \tag{11}$$

The following parameters describing fine Co particles were taken: the magnetic moment on Co atom $m_{Co} = 1.62\ \mu_B/atom$; fcc-Co lattice constant $a = 3.545$ Å, that gives the saturation magnetization $M_s = 1349$ emu/cm^3; uniaxial anisotropy constant $K_1 = 4.53\times10^6$ erg/cm^3 (whence one gets $H_0 = 3358$ Oe), exchange stiffness constant $A = 2.8\times10^{-6}$ erg/cm (experimental value for nanocrystalline Co samples, according to Ref. 15). Then for a ferromagnetic exchange length we get $L_{ex}^0 = 78.6$ Å.

4. Results and Discussion

The typical experimental and theoretically calculated hysteresis loops are shown in Fig. 1. The theoretical loop fits well experimental one, it is a sum of hysteresis loop due to single domain particles and magnetization curve due to superparamagnetic particles. The calculated particle size distribution is presented in Fig. 2. The first and the second peaks correspond to superparamagnetic and single domain particles, respectively.

The SiO$_2$-based samples consisting fine Co particles (see section 2) are used as catalysts of chemical reactions [16]. Of crucial interest for sample manufacturers was to find the influence of reduction, oxidation and other technological conditions on quantity balance between superparamagnetic and single domain ferromagnetic particles. The presented method for evaluation of the particle size distribution can serve for this goal.

Consider first the sample series r5, r13, r14, r22, r30, r62. These samples were reduced from Co$_3$O$_4$/SiO$_2$ systems in the hydrogen atmosphere (see section 2 for details) in

Fig. 4. The ratio V_{sp}/V_{sd} of fraction volumes of superparamagnetic and single domain particles vs degree of oxidation for series r100ox51, r100ox56, r100ox71, r100ox89; last number designates the degree of oxidation. Dashed line is guide for eye.

the various degree (which is designated by number for given sample). Fig. 3 shows the ratio of fraction volumes (they are proportional to saturation magnetizations) vs degree of reduction. In the process of reduction growth rate of superparamagnetic particles is larger, than growth rate of single domain ferromagnetic particles

The ratio of fraction volumes vs degree of oxidation for series of samples r100ox51, r100ox56, r100ox71, r100ox89 is shown in Fig. 4. The conclusion here is that oxidation of superparamagnetic particle goes faster than oxidation of single domain Co particles. The results for relative reduction and oxidation rates for different fractions of particles obtained here are in agreement with conclusion of Ref. 16 based on thermodynamics arguments.

The distributions of volume fraction of particles ($\sim P(d)$ $*d^3$) for samples 73H300 and 73HO300 are presented in
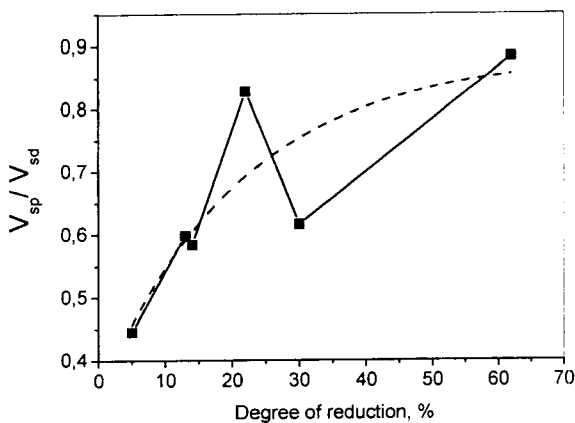

Fig. 3. The ratio V_{sp}/V_{sd} of fraction volumes of superparamagnetic and single domain particles vs degree of reduction for series r5, r13, r14, r22, r30, r62. Dashed line is guide for eye.
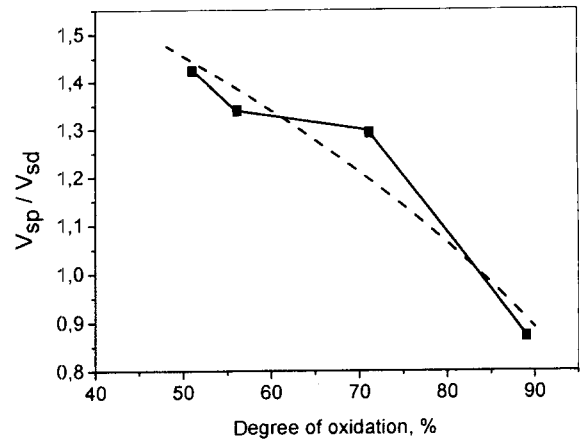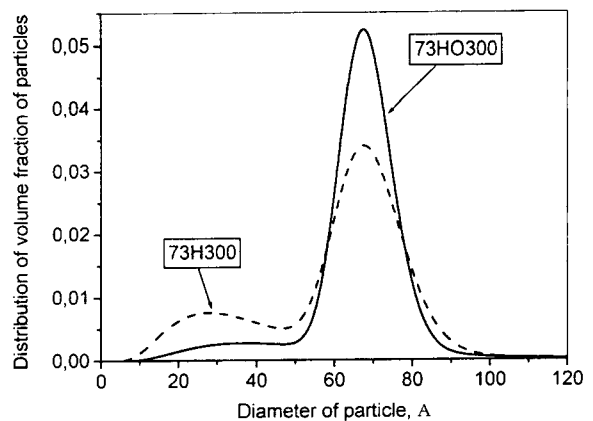

Fig. 5. Distribution of volume fraction of particles for samples 73HO300 and 73H300, reduced in mixture of hydrogen with water vapor and in pure hydrogen, accordingly.
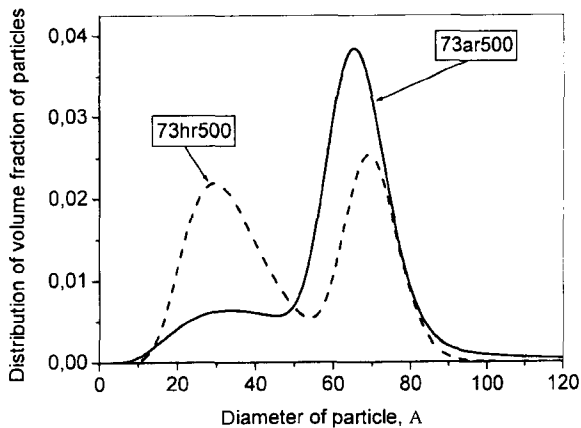
Fig. 6. Distribution of volume fraction of particles for samples 73ar500 and 73hr500, reduced in mixture of 95%Ar+5%H$_2$ and in pure hydrogen, accordingly.

Fig. 5. These samples were reduced at 300 K in pure hydrogen and in mixture of hydrogen with water vapor, respectively. The areas under two peaks of distributions shown in Fig. 5 are proportional to fraction volumes of particles for the given sample. For the sample 73HO300 the peak of distribution function corresponding to single domain particles is higher, than the same peak for the sample 73H300, and, accordingly, the peak corresponding to superparamagnetic particles is lower, than one for the sample 73H300. Hence, addition of water vapor into hydrogen atmosphere increases the fraction volume of single domain particles.

The distributions of volume fraction of particles for samples 73ar500 and 73hr500 are shown in Fig. 6. The sample 73ar500 was reduced at 500°C in 95%Ar+5%H$_2$ atmosphere; 73hr500 was reduced at the same temperature but in pure hydrogen. The presence of argon in gas mixture affects on the ratio of fraction volumes the same way as water vapor being found in gas mixture; however, this influence is more pronounced (see Fig. 6).

The measurements also have been done on the series of samples reduced from Co oxides in 95%Ar+5%H$_2$ atmosphere at different temperatures (350°C÷500°C). The ratio of fraction volumes versus temperature is shown in Fig. 7. This ratio increases with reduction temperature T. Therefore, one can conclude that temperature influences the chemical reaction such a way that at higher T the reduction rate of small superparamagnetic particles is higher in comparison with the reduction rate of larger single domain particles.

In conclusion, we have presented a simple method for evaluation of the particle size distribution of ultrafine-particles from hysteresis loop measurements. The method allowed us to investigate the influence of different prepa-
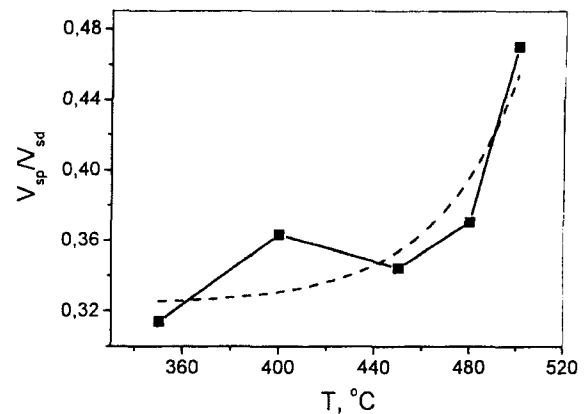

Fig. 7. The ratio V_{sp}/V_{sd} of fraction volumes of superparamagnetic and single domain particles vs temperature for sample series 73ar350, 73ar400, 73ar450, 73ar480 and 73ar500 (the last number designates temperature). Dashed line is guide for eye.

ration conditions onto particle size distribution function for the SiO$_2$-based Co nanoparticle systems. In particular, it has been shown that reduction and oxidation rates of small superparamagnetic nanoparticles are higher compared to that of larger single domain particles. The deeper insight into the illustrated mechanisms of chemical reactions will be given in the forthcoming publication.

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