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Investigation of the Co particle size distribution in ensembles produced by reduction from Co oxide

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Abstract

We outline the method for evaluation of the particle size distribution of the magnetic nanoparticles from the hysteresis loop measurements. We apply the method to study the ultrafine Co particles filling the porous silica gel matrix (SiO_2). The influence of the technological conditions of the sample preparation onto particle size distribution function is demonstrated.

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1. Introduction

The investigation of the properties of magnetic ultrafine particle systems has attracted a lot of attention during the last two decades because of continuous broadening of the area of application of new magnetic materials [1]. A lot of factors determine the properties of these systems such as surface and quantum size effects for small particles and clusters, transition from the single-domain to super-paramagnetic regime and interparticle interactions. In the given report we outline a simple method for the evaluation of the particle size distribution of the magnetic ultrafine particle systems using the magnetization loops measurements. We apply this method to study Co nanoparticles filling the porous silica gel matrix (SiO₂).

2. Sample preparation

The samples consisting ultrafine Co particles were produced using the porous material (silica gel) with surface density 73 m^2/g and porous size about 40 nm which was filled by the solution of Co nitrate $Co(NO_3)_2$. 6H₂O. After impregnation the samples were dried in the air atmosphere at 120°C within 4 h, and then were annealed at 500°C within 6 h. Thus, the Co_3O_4/SiO_2 systems with 10 at % Co were obtained. The pure cobalt was being reduced from the oxide leading to the formation of fine Co particles. The reduction was performed at different temperatures and in different gas mixtures such as pure hydrogen, the mixture of water vapor and hydrogen, or 2% H₂ + 98% Ar atmosphere. The cell of vibrating magnetometer was used as a reactor that allowed controlling the magnetization of a sample. Magnetization was assumed to be proportional to the weight of metal Co.

3. Evaluation of the particle size distribution

The hysteresis loops of the prepared samples have been measured using vibrating sample anisometer. The

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Fig. 1. Typical experimental and calculated hysteresis loops for fine Co particle system and calculated particle size distribution (at room temperature).

experimental set-up was described earlier [2]. The analysis of the hysteresis loops (typical example is shown in Fig. 1) allowed us to conclude that two types of nanoparticles are present in the silica gel matrix; namely superparamagnetic particles with small grain sizes and single-domain particles having larger grain sizes. This conclusion is based on the observations that (i) hysteresis loops are nonsaturated in large magnetic fields (up to 8000 Oe) which is a typical behavior for systems consisting superparamagnetic particles, and (ii) the hysteresis loops have residual magnetization, thus not all particles are superparamagnetic.

To evaluate the particle size distribution, we assumed that both "small" and "large" particles have the spherical form and considering that two fractions of particles are independent subsystems, we presented the particle size distribution P(d) as a sum of two log-normal distributions $f_1(d)$ and $f_2(d)$. The contribution of the small superparamagnetic particles to the hysteresis loop is described by the Langevin function averaged over distribution $f_1(d)$ [3]. We describe the second fraction (large particles) by the Stoner-Wohlfarth model [4] for non-interacting single-domain particles with uniaxial magneto-crystalline anisotropy and easy axis oriented randomly in space. The dependence of coercivity $H_c \sim d^6$ on the grain size d was taken into account as it was predicted by the random anisotropy model [5,6]. Parameters describing two log-normal distributions are determined using the numerical procedure of minimization of a root-mean-square deviation between the theoretical and experimental loops. The typical experimental and calculated fitting hysteresis loops are shown in Fig. 1a. The corresponding particle size distribution (Fig. 1b) has two peaks that reflect the non-homogeneous structure of the samples, so that the first peak corresponds to subsystem of the superparamagnetic particles and the second one corresponds to the singledomain particles.



Fig. 2. The ratio V_{sp}/V_{sd} of volume fraction of superparamagnetic and single-domain particles vs. temperature of reduction.

4. Results and discussion

One of our aims was to find such technological conditions that would allow getting samples containing larger quantity of superparamegnetic particles, because small Co particles serve as catalysts of chemical reactions. For this goal first the series of samples reduced from Co oxide in hydrogen atmosphere at different temperatures (270-550°C) was prepared. We observed that the ratio of volume fraction of superparamagnetic and single-domain particles increases while the temperature of reduction process increases (Fig. 2). At the first step of the reduction the impurity centers (small Co clusters) appear in the Co oxide. The subsequent growth of the Co particles takes place around impurity centers. The velocity of this process is weakly dependent on the temperature. However, the increase of temperature leads to the more active formation of the impurity centers thus leading to the growth of the volume fraction of the small superparamagnetic particles.



Fig. 3. Distribution of volume fraction of particles: (a) samples 73HO300 and 73H300 and (b) samples 73ar500 and 73hr500.

We also studied the samples prepared by reduction from the Co oxide using different gas atmosphere. The distributions of volume fraction of Co particles $(\sim P(d)d^3)$ for samples marked as 73H300 and 73HO300 are presented in Fig. 3a. These samples were reduced at 300°C in pure hydrogen and in the mixture of hydrogen with water vapor, respectively. The areas under two peaks of distributions shown in Fig. 3a are proportional to volume fractions of particles. We conclude that addition of water vapor into hydrogen atmosphere increases the volume fraction of singledomain particles. The similar tendency (the increase of the volume fraction of the single-domain particles, while decreasing the partial pressure of hydrogen in the gas mixture used for reduction of Co particles) we observed for two samples marked as 73ar500 and 73hr500 (Fig. 3b) which were reduced at 500°C in 95% Ar + 5% H₂ atmosphere and in pure H₂. The explanation of such a behavior was given in Ref. [7]. It follows from the thermodynamic consideration of the chemical process [7] that the reduction of smaller particles requires larger partial pressure of hydrogen.

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