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Magnetic characterization of cobalt nanoparticles by temperature-dependent magnetic relaxation measurements

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A recently introduced method for the characterization of magnetic nanoparticles based on the analysis of the dependence of the Néel relaxation signal on the sample temperature (temperature-dependent magnetorelaxometry, TMRX) has been applied to characterize air-stable cobalt particles made by decomposition of $Co_2(CO)_8$ in the presence of aluminium-organic compounds. The influence of small changes in the preparation process on the magnetic relaxation behaviour has been studied.

A mean magnetically relevant particle size has been derived from TMRX, zero-field cooled magnetisation and low-temperature coercivity measurements and has been compared with a mean physical size determined by transmission electron microscopy investigations. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: air-stable magnetic cobalt nanoparticles; aluminium-organic compounds; temperature-dependent relaxation measurements; Néel relaxation; zero-field cooled magnetization measurements; low-temperature coercivity measurements

INTRODUCTION

The magnetic properties of ferrofluids are strongly influenced by the distribution density of energy barriers E in these many-particle systems. In the simplest case, when the interparticle interaction can be neglected, this energy barrier distribution can be calculated from the distributions of the magnetic anisotropy constant K and the volumes V of the single particles, because E can be approximately calculated as the product of K and V (in this model K describes the effective anisotropy constant of these single-domain particles resulting in a general case from shape, crystallographic, and/or surface anisotropies). However, the measurement of these parameters using common methods such as atomic force microscopy, transmission electron microscopy (TEM) or their determination by the analysis of magnetization curves are very elaborate and need additional assumptions or *a priori* knowledge of the particle size distribution. In contrast to these methods, the evaluation of the temperature dependence of the Néel relaxation signal provides direct access to the distribution of the energy barriers E as one of the most important parameters of this system.[1–4] The investigation of strongly diluted ferrofluids, where an interaction between particles can be neglected (providing that the particles are not aggregated), enables the determination of magnetic parameters of the single particles.

In this paper we report on the investigation of recently developed magnetic cobalt nanoparticles.[5] So far, such particles have been analysed using high-resolution TEM (HRTEM),[6,7] X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and electron spectroscopies (ultraviolet photoelectron spectroscopy, metastable impact electron spectroscopy).[8] We have investigated cobalt nanoparticles using the temperature-dependent magnetorelaxometry (TMRX) method[9] with respect to the

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effects of small changes in the preparation process on the magnetic relaxation behaviour of the particles. Additionally, we have applied zero-field cooled (ZFC) magnetization and low-temperature coercivity measurements to determine the magnetic anisotropy and the magnetization behaviour of the particles.

MATERIAL AND METHODS

Magnetic particles and sample preparation

Air-stable cobalt particles as the precursors for the preparation of magnetic fluids have been made by decomposition of $Co_2(CO)_8$ in the presence of aluminium-organic compounds, modification of the protective shell by the smooth oxidation of the surface of Co/AlR_3 particles. The cobalt particles obtained in the powder and in the fluid remain stable under air and retain their magnetic properties for a long time. Owing to variations in the technological process we were able to produce particles showing different magnetic behaviours. In principle, three different types of cobalt particle could be investigated:

1. Cobalt particles made in the presence of $Al(C_8H_{17})_3$, initial ratio Co : Al = 10 : 1 (cobalt powders 4 and 5).
2. Cobalt particles made in the presence of $Al(C_8H_{17})_3$, initial ratio Co : Al = 5 : 1 (cobalt powder 3).
3. Cobalt particles made in the presence of $Al(C_2H_5)_3$, initial ratio Co : Al = 10 : 1 (cobalt powders 1 and 2)

Figure 1 illustrates the synthesis procedure of air-stable cobalt particles in powder under consideration of the technological variations.

These cobalt particles can be used as magnetic powder itself for many advanced technologies, as well as for precursors of magnetic particles for the preparation of magnetic fluids.

Preliminary experiments show, that cobalt powder obtained in the presence of $Al(C_8H_{17})_3$ can be peptized by suitable surfactants in toluene, kerosene, vacuum oil L9 and silicone oil DC-702.

MAGNETIC MEASUREMENTS

Temperature-dependent magnetic relaxation measurements

Theoretical

In our experimental investigations we use the main result of Berkov and Kötitz[2]: the magnetization relaxation of a system with the energy barrier distribution $\rho(E)$ (after this system has been magnetized in a weak external field for a finite time t_{mag}) can be described as

$$M(t) = kT\rho(E^{max})\delta m(E^{max}) \log\left(1 + \frac{t_{mag}}{t}\right) \qquad (1)$$

Hence, the relaxation amplitude M_0 in the expression $M(t) = M_0 \log(1 + t_{mag}/t)$ (see below) is simply proportional to the height of the energy barrier distribution $\rho(E^{max})$ at the known energy $E^{max} \approx kT \log(\tau_{mag})$:

$$M_0 = kT\rho(E^{max})\delta m(E^{max}) \qquad (2)$$

This means that by measuring the magnetization relaxation for the given temperature T and magnetization time τ_{mag} and fitting the obtained dependence by the $\log(1 + t_{mag}/t)$ curve we can directly obtain the height of the energy

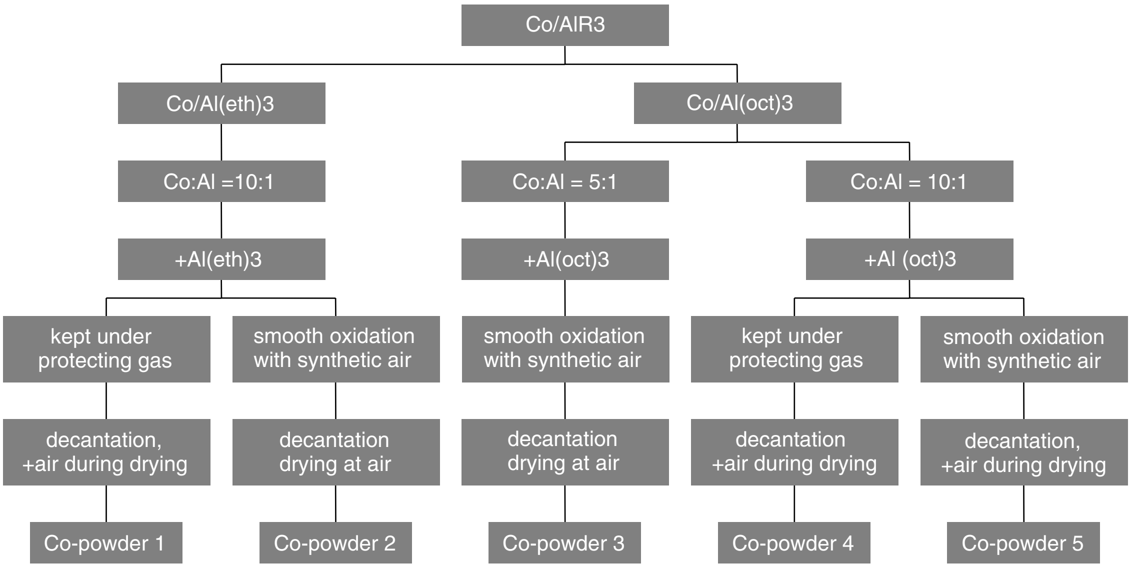

Figure 1. Scheme of the preparation of cobalt particles for powders and magnetic fluids using different types of aluminium-organic compounds ($Al(C_8H_{17})_3$ and $Al(C_2H_5)_3$), different initial Co : Al ratios and different conditions of oxidation.

barrier distribution $\rho(E)$ multiplied by the corresponding magnetization change $\delta m(E)$. This product is the most important characteristic of the magnetic system when we are interested in its equilibrium and non-equilibrium thermodynamical properties.

Experimental

The measurement setup for TMRX of immobilized cobalt nanoparticles consists of a second-order SQUID gradiometer to measure the magnetic relaxation signal, Helmholtz coils to magnetize the sample, and a Pt100 platinum thermometer to determine the sample temperature. This experimental setup allows us to determine the magnetization relaxation signal of magnetic nanoparticles (MNPs) over a range from 77 to 350 K (Fig. 2).[9]

To extract the necessary information reliably from our measurements, we have used Eqn (1), where the time decay of the sample magnetization $M(t)$ due to the Néel relaxation can be described by

$$M(t) = M_0 \ln\left(1 + \frac{t_{\text{mag}}}{t}\right) \tag{3}$$

where M_0 is the magnetization at $t/t_{\text{mag}} = 1/(\mathrm{e} - 1)$. For a more detailed description of the system see Romanus *et al.*[9]

ZFC magnetization curves

As the TMRX measurement method is restricted to a temperature range of 77 to 350 K at the current state of development, and the signal maximum of certain samples seems to appear at greater temperatures, we needed an additional method to determine this signal maximum.[10,11] Hence, we measured a ZFC magnetization curve, i.e. the magnetic moment in a constant weak magnetic field (1 mT) versus temperature after demagnetization of the sample. The heating rate chosen was 5 K min^{-1}.

Low-temperature coercivity measurements

To extract information about the mean anisotropy of the particles from magnetic measurements one can determine the magnetic coercivity $H_C = H_K = 2K/M_S$ at temperatures lower than the blocking temperature of the particle system if the easy axis is parallel to the applied field. Here, H_K is the anisotropy field, K the anisotropy constant and M_S the saturation magnetization of the particle. Assuming a many-particle system, where the easy axes are oriented randomly, and ignoring the particle interaction, the coercivity is given by $H_C = 0.479H_K$ and the remanence M_R is defined as $M_R \approx 0.5M_S$ for particles with a uniaxial magnetic anisotropy K_u. For particles with a pure cubic anisotropy the values of M_R/M_S are 0.83 and 0.87 for positive and negative anisotropy respectively.[12,13]

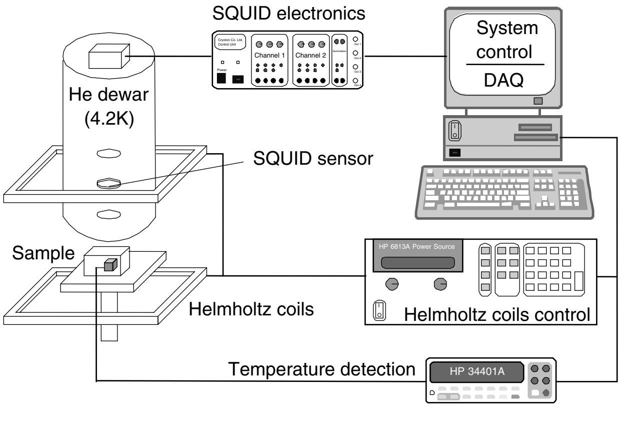

Figure 2. Scheme for the TMRX measurement system.

RESULTS AND DISCUSSION

Owing to variations in the preparation process we have found three types of particles, each showing a different magnetic relaxation behaviour (for preparation details see the 'Material and Methods' section above): (I) cobalt powders 4 and 5; (II) cobalt powder 3; (III) cobalt powders 1 and 2.

Figure 3 illustrates the different relaxation behaviour by means of the relaxation amplitude versus temperature curve. One sample of each group was chosen to explain the principal magnetic behaviour of this group. As the samples have not been set up to contain the same amount of cobalt, we have normalized the curves to the maximum amplitude in the measured temperature interval for better comparability. The magnetic relaxation behaviour can be described as follows. The first group of particles (circles) exhibits a first signal maximum at about 230 K, at the end of the temperature interval we again find an increase of the amplitude, probably leading to a second maximum at higher temperatures. The second group (triangles) has its maximum at temperatures beyond the accessible temperature interval. The third group (squares) shows only one signal maximum at about 150 K and

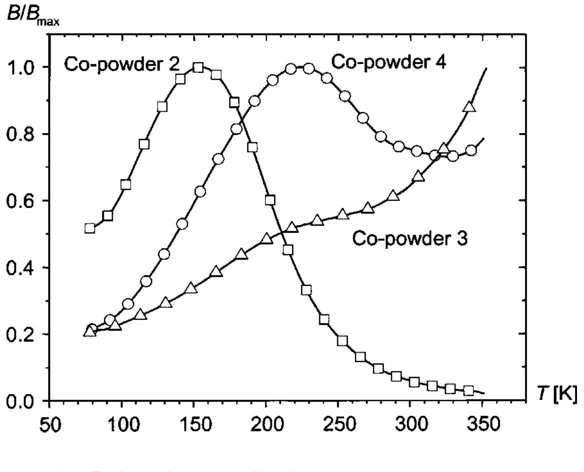

Figure 3. Relaxation amplitude versus temperature curve of three samples illustrating the principal relaxation behaviour of the three groups of cobalt particles.

the amplitude decreases to zero at the end of the temperature interval.

Under consideration of the time constant for Néel relaxation processes

$$t_{\text{Néel}} = t_0 \, e^{KV/k_B T} \tag{4}$$

where t_0 is usually quoted as 10^{-10} s and $t_{\text{Néel}}$ has to be set equal to our measurement time of 1 s, it is possible to recalculate the temperature axis into an energy axis (KV). For simplification one can estimate

$$KV[\text{J}] \cong 23 k_B T \simeq 3.2 \times 10^{-22} T[\text{K}] \tag{5}$$

Furthermore, we have measured other samples prepared later under the same conditions. In all cases the measured TMRX curves of the samples show the typical structure of the corresponding preparation group. Hence, we conclude that the preparation technology is highly reproducible and the main parameters determining the magnetic properties of the particles are the cobalt-to-aluminium ratio and the kind of the aluminium-organic compound.

To determine the expected maxima at higher temperatures for the samples of group II we measured ZFC magnetization curves of the corresponding samples. The ZFC magnetization curve of cobalt powder 3 (group II) is shown in Fig. 4. For comparison, in Fig. 5 we show the ZFC curve of sample cobalt powder 2 (group III), where the maximum corresponds very well with that of the TMRX measurement.

The ZFC magnetization curves reveal typical features of a small-particle system. The maxima of the curves at $T = 485$ K (cobalt powder 3) and $T = 175$ K (cobalt powder 2) mark the transition from stable single-domain particles to superparamagnetic ones. $T_{\max}$ is proportional to the mean blocking temperature and is influenced by the width of the particle size distribution.[14] The small peak at $T = 580$ K (cobalt powder 3) corresponds to an irreversible phase transition shown by differential thermal analysis–thermogravimetry (DTA–TG), and is for that reason not interpreted as a second maximum in the particle distribution.

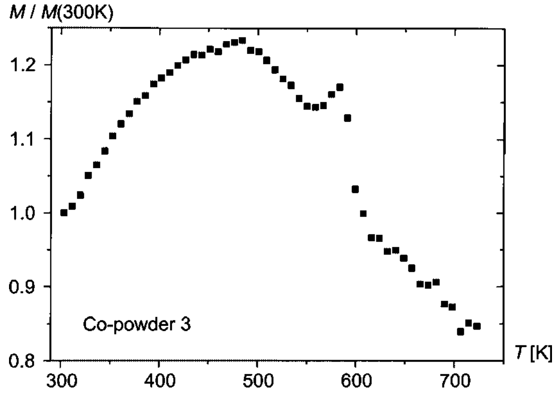

Figure 4. ZFC magnetization curve of sample cobalt powder 3 in a temperature range from 300 to 730 K (measuring field 1 mT). The magnetization amplitude has been normalized to its 300 K value.

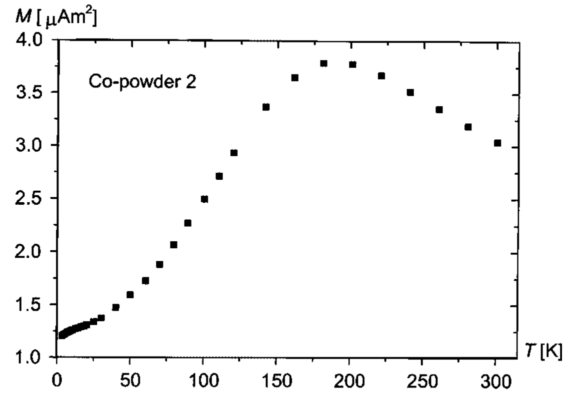

Figure 5. ZFC magnetization curve of sample cobalt powder 2 in a temperature range from 4 to 300 K (measuring field 1 mT).

To obtain an effective anisotropy constant K of the particles we made low-temperature coercivity measurements as described above. Figure 6 shows an example curve obtained.

Applying $H_C \simeq K/M_S$ for our system with a measured $H_C = 0.27\ \text{V s m}^{-2}$ for sample cobalt powder 2 at $T = 4$ K and setting $M_S = 1.4 \times 10^6\ \text{A m}^{-1}$ as the value of bulk cobalt, we obtain a mean value of $K = 3.78 \times 10^5\ \text{J m}^{-3}$. Similar measurements of cobalt powder 3 yielded $K = 1.8 \times 10^5\ \text{J m}^{-3}$. In all cases we measured an M_R/M_S ratio of about 0.5 at 4 K. Thus, a uniaxial anisotropy plays a dominant role in the magnetization process. Structural investigations with EXAFS and XANES[8] revealed a dominating f.c.c. structure for the particles investigated.

Using these calculated anisotropy constants, on approaching the energy barrier KV (Eqn (5)), where T has been set to

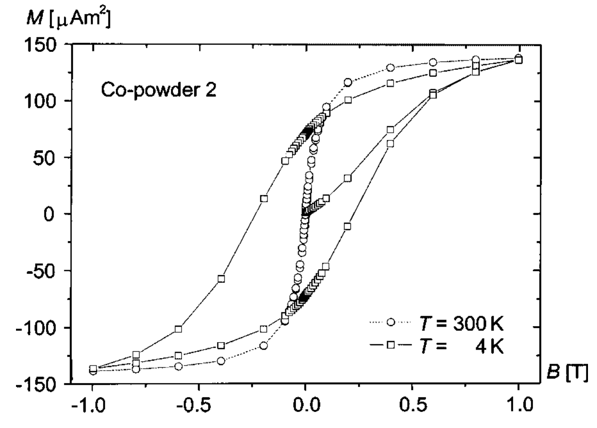

Figure 6. Low-temperature magnetization curve to extract the coercivity. The magnetization curve at 300 K illustrates the superparamagnetic behaviour of the particles.

Table 1. Summarized results of two selected samples obtained by magnetic investigations. A derived 'magnetic' particle diameter is compared with a physical one determined by TEM investigations

Sample	Co powder 2	Co powder 3
Structure	$Al(C_2H_5)_3$	$Al(C_8H_{17})_3$
Co : Al ratio	10 : 1	5 : 1
H_C at 4 K (T)	0.27	0.13
M_R/M_S at 4 K	0.49	0.48
K (J m^{-3}) ($M_S = 1.4 \times 10^6$ A m^{-1})	3.8×10^5	1.8×10^5
Max TMRX (K)	155	>350
Max ZFC (K)	180	470
d_{mag} (nm)	6.5	11.5
d_{TEM} (nm)	6.5 ± 1.5	10 ± 1.6

the temperature at the signal maximum, we were able to estimate the magnetic core volumes of the particles. Assuming spherical particles for simplification and M_S of bulk cobalt, the estimations yielded magnetic core diameters of 11.5 nm for cobalt powder 3 and 6.5 nm for cobalt powder 2. An interesting result of this measurement is that the anisotropy of the particles of cobalt powder 3 (with a larger magnetic diameter) is smaller than the anisotropy of particles of cobalt powder 2. This is in agreement with investigations on other magnetic particles, e.g. on iron particles with diameters in the same region.[15] This can be explained by an increasing influence of surface and shape anisotropy in smaller particles.

The reason for these very different values for the magnetic diameters of powders 3 and 2 particles, i.e. 11.5 nm and 6.5 nm respectively, is not clear yet. Investigations of the particles using TEM yield particle core diameter distributions of 10.0 ± 1.6 nm for powder 3 and 6.5 ± 1.5 nm for powder 2 (see Table 1). Furthermore, the structural investigations[8] show that, under the preparation conditions for group III (powder 2), a shell of nonmagnetic cobalt compounds arises on the surface of the particles. In contradiction, the particles of this group show a clear f.c.c. structure. For a more detailed interpretation, further investigations would be necessary.

CONCLUSIONS

A recently introduced method for the characterization of MNP based on the analysis of the dependence of the Néel relaxation signal on the sample temperature has been applied to characterize air-stable cobalt particles made by decomposition of $Co_2(CO)_8$ in the presence of aluminium-organic compounds. The influence of small changes in the preparation process on the magnetic relaxation behaviour has been studied. It could be shown that the TMRX curves are a proper qualitative and quantitative 'fingerprint' of magnetic particle systems. The results also confirm the reproducibility of the preparation method applied. Samples prepared under the same conditions yield the same structure and comparable parameters of the TMRX curves. A mean magnetically relevant particle size has been derived from TMRX, ZFC and low-temperature coercivity measurements and has been compared with a mean physical size determined by TEM investigations. The results of two selected samples for different preparation conditions are summarized in Table 1.

It seems to be typical that particles prepared under addition of $Al(C_8H_{17})_3$ (group III, cobalt powder 2) have remarkably larger magnetic diameters than particles prepared using $Al(C_2H_5)_3$ (group II, cobalt powder 3).

For more detailed structural and quantitative analysis, further investigations would be necessary.

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