Magnetic properties of FeCo nanoparticles encapsulated in carbon

M. Maryško¹, R. Fajgar², J. Šubrt³, N. Murafa³, K. Knížek¹

¹Institute of Physics of ASCR, v.v.i, Na Slovance 2, 182 21 Praha 8, Czech Republic
²Institute of Chemical Process Fundamentals, ASCR, 16502 Prague, Czech Republic
³Institute of Inorganic Chemistry, ASCR, 25068 Rež, Czech Republic

E-mail: marysko@fzu.cz

Abstract. The as-prepared and heat treated iron/cobalt nanoparticles with r = Co/Fe = 0.08
and 1 were obtained by laser decomposition. At low temperatures all the materials are in a
ferromagnetic blocked state. At higher temperatures (T > 200 K) the as-prepared materials
exhibit superparamagnetic properties. In this case the nanoparticle size distribution deduced
from the m(H) curves and from the difference between the FC and ZFC susceptibilities was
compared with the TEM data. The heat treated materials have larger magnetizations and a
maximum (161 emu/g) was achieved for the r=1 material heat treated at 900°C. For this material
an anomalous form of the hysteresis loop was explained in terms of a superposition of single
and multi-domain magnetizations.

1. Introduction
Metallic ferromagnetic nanoparticles are intensively studied with regard to their potential
applications as magnetic storage media, biosensors and carriers for drug targeting [1,2].
Encapsulation of the nanoparticles by carbon shells improves the stability of the nanoparticles
and ensures the biocompatibility of these materials. In this work the magnetic properties of
the FeCo nanoparticles encapsulated by carbon will be studied. The nanoparticles with the
atomic ratios Co/Fe = 0.08 and 1 were prepared by laser induced deposition. The very
nanoparticles are ferromagnetic but the resulting powder nanomaterial represents a ferromagnet
or superparamagnet depending on the particle size. We shall focus our attention on the magnetic
properties of the FeCo nanoparticles and comparison with the morphological data obtained by
TEM method.

2. Experimental
Two series of the FeCo alloy nanoparticles encapsulated in carbon with the atomic ratios
Co/Fe = 0.08 and 1 and chemical compositions Fe1Co0.12C7.25 and Fe1Co0.98C6.9 respectively
were prepared by ArF laser-induced decomposition from the gaseous acetylene - Fe(CO)5-
Co(CO)3(NO)mixture. The samples in the as-prepared state and after annealing at T-an= 600 ,
900 and 1150°C were denoted by the symbols 08/AP, 08/600, 08/900, 08/1150 and 1/AP, 1/600,
1/900, 1/1150 for r=0.08 and r=1 respectively. The morphology of the deposited materials was
studied by High resolution electron microscopy (HRTEM) using a microscope (JEOL). Images
were recorded on a CCD camera (Gatan) with resolution 1024 x 1024 pixels. The magnetization
Table 1. Magnetizations for $H = 30$ kOe, coercivity $H_c$ and exchange bias $H_{EB}$.

| Sample  | $m(300\text{K})(\text{emu/g})$ | $m(5\text{K})(\text{emu/g})$ | $H_c(300\text{K})(\text{Oe})$ | $H_c(5\text{K})(\text{Oe})$ | $H_{EB}(\text{Oe})$ |
|---------|---------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------|
| 08/AP   | 60                              | 74                            | 0                             | 300                           | 5                   |
| 08/600  | 97                              | 104                           | 155                           | 788                           | 67                  |
| 08/900  | 84                              | 89                            | 400                           | 793                           | 50                  |
| 08/1150 | 86                              | 89                            | 250                           | 362                           | 5                   |
| 1/AP    | 39                              | 51.5                          | 0                             | 933                           | 113                 |
| 1/600   | 155                             | 158                           | 314                           | 965                           | 47                  |
| 1/900   | 161                             | 163.5                         | 145                           | 171                           | 0                   |
| 1/1150  | 146                             | 148                           | 152                           | 439                           | 5                   |

Figure 1. TEM images for the samples a) 08/AP (scale 50 nm) and b) 08/1150 (scale 100 nm).

Figure 2. Temperature dependences of the coercivity.

Measurements were carried out in the temperature region 5-300 K using a SQUID magnetometer MPMS-5S (Quantum Design). The basic information on the magnetic state was obtained from the hysteresis loops. These $m(H)$ curves were recorded between -30 and 30 kOe after cooling the samples from 300 K in zero field. The exchange bias $H_{EB}$ was measured at $T = 5$ K after cooling the sample in field 30 kOe. For the as-prepared samples the $m(H)$ curves between 0 and 50 kOe were measured between 150 and 300 K. The susceptibility study was performed by measuring $m/H$ ratio in zero field (ZFC) and field-cooled (FC) regimes for different magnetic fields.
3. Results

In Fig.1 the low magnification TEM images for 08/AP and 08/1150 are shown which enable us to roughly estimate average nanoparticle diameters 3 and 25 nm respectively. The same diameters i.e. \( D(\text{AP}) \approx 3 \) and \( D(1150) \approx 25 \) nm was obtained for the Co/Fe = 1 samples but in this case the width of the distribution was evidently larger. The HRTEM images not presented here show a high quality of the carbon encapsulation. The hysteresis loops measured in the temperature region 5 - 300 K yielded information on the basic magnetic properties of the samples as are the saturation magnetization \( m_s \approx m(H=30 \text{ kOe}) \), coercivity \( H_c \) and exchange bias \( H_{EB} \). These data are summarized in Tab.1. With the exception of the sample 1/900 \( H_c \) at \( T=5 \) K is relatively large and its value decreases with increasing temperature (Fig.2). Here, it can be seen that at \( T > T_{B_{max}} \) \( H_c \approx 0 \), which suggests the presence of the superparamagnetic (SPM) state at higher temperatures. For 08/AP and 1/AP we have \( T_{B_{max}} = 30 \) and 150 K respectively. This temperature reflects a maximum blocking temperature corresponding to the largest nanoparticles. The presence of the superparamagnetism at higher temperatures can be verified by measuring the \( m(H) \) curves up to \( H = 50 \) kOe. In this case the superparamagnetic magnetization \( m_{SPM} \) was obtained after subtracting a linear term \( \chi_a \) \( H \). The value of \( \chi_a \) was determined by fitting \( m \) to the expression \( m=m_\infty(1.-a/H)+\chi_a H \), where \( m_\infty \) is the saturated superparamagnetic magnetization and \( a \) a fitting constant. In molecular field approximation \( a=kT/\mu \), where \( \mu \) is the magnetic moment of the nanoparticle and this proportionality was also verified in our fitting process. For the sample 08/AP \( \chi_a \) increases from \( 2.26 \times 10^{-5} \text{ emu}/(\text{g.Oe}) \) at 125 K to \( 3.4 \times 10^{-5} \text{ emu}/(\text{g.Oe}) \) at 300 K. For 1/AP \( \chi_a \) increases from \( 3.67 \times 10^{-5} \text{ emu}/(\text{g.Oe}) \) at 250 K to \( 3.86 \times 10^{-5} \text{ emu}/(\text{g.Oe}) \) at 300 K. If we now evaluate the reduced value of the SPM magnetization \( m_{SPM}/m_\infty \) as a function of \( H/T \) we see that for samples 08/AP (\( T \geq 150 \) K) and 1/AP (\( T \geq 250 \) K) the curves superimpose. In Fig.3 the influence of the annealing on the low temperature hysteresis curve ( \( T = 15 \) K) is shown for the Co/Fe = 1 samples. We find an anomalous constricted form of the \( m(H) \) curve for the sample 1/900 annealed at 900\(^0\) C. No such behaviour was observed for the Co/Fe = 0.08 samples.

4. Discussion

4.1. As-prepared samples

In the SPM region the dependence \( m_{SPM}(H) \) can be fitted to that obtained as a sum of Langevin functions using a standard log-normal particle diameter distribution \( w(D) \)[3]. For the 08/AP sample this yields the mean (magnetic) diameter \( D_{mag}=3.07 \) nm with the standard deviation \( \text{StdDev}(D)=0.78 \) nm (\( \sigma=0.25 \)). For 1/AP the same procedure gives \( D_{mag}=3.44 \) nm, \( \text{StdDev}(D)=1.32 \) nm (\( \sigma=0.37 \)). The corresponding log-normal distributions of particle diameters are shown in Fig.3a,b. The diameters \( D_{mag} \) are in a qualitative agreement with those observed on the TEM images. The distribution of the blocking temperatures \( w(T_B) \) derived from the temperature derivative of the difference between ZFC and FC susceptibility [4] can be compared with the log-normal distribution \( w(D) \) for a given value of \( \sigma \) (Fig.4a,b). Here we see that the distribution \( w(T_B) \) can be well approximated by the log-normal function only in for the 08/AP sample. In the case of the 1/AP sample the distribution \( w(T_B) \) differs from the log-normal type in the region of large \( T_B \), i.e. for large nanoparticles. For the blocking temperature proportional to the volume of the nanoparticle \( V=\pi D^3/6 \) the parameter \( \sigma_{T_B} \) should be given by \( 3 \sigma_D \). In Fig.4a,b this comparison has been made for \( \sigma = 0.75 \) and 1.11 for 08/AP and 1/AP respectively. Using these values \( \sigma_{T_B} = 3 \sigma_D \) we find that the calculated \( w(T_B) \) distribution is in both cases wider than that deduced from the ZFC, FC susceptibilities. For 08/AP a relatively good agreement was found for \( \sigma_{T_B}=0.45 \) and for 1/AP we may estimate \( \sigma_{T_B} \approx 0.5 \). For 08/AP the value \( \sigma_{T_B} \) is not far from the value \( 2\sigma_D \). This result could be understood if we admitted that the anisotropy energy of the nanoparticle is predominantly given by the surface contribution [5]. The interesting experimental fact is the presence of a linear term \( \sim \chi_a H \), which increases


Figure 3. Log-normal distributions on the nanoparticle diameters deduced from the reduced SPM magnetizations with the log-normal courses for different values of $\sigma_{TB}$.

Figure 4. Distributions of the blocking temperatures evaluated from the ZFC and FC susceptibilities (open circles) compared with the log-normal courses for different values of $\sigma_{TB}$.

4.2. annealed samples
For these samples, e.g. for 08/1150 and 1/1150 we estimated the nanoparticle diameter using the proportionality $T_B \sim E_A$ (anisotropy energy) and the formula for $H_c(T)$ valid for noninteracting single-domain particles [6]. The agreement with the TEM diameter 25 nm can be achieved using the surface anisotropy model mentioned above. An anomalous hysteresis loop of the sample 1/900 can be explained assuming the simultaneous presence of single and multi-domain nanoparticles. The superposition of the rectangular for multi-domain and single-domain $m(H)$ curves really agrees with the observed hysteresis loop (Fig. 4b). This interpretation is also supported by the form of the virgin magnetization curve found for the sample 1/900 (Fig.4a).

5. Conclusions
For the as-prepared samples the average diameter of the nanoparticle deduced from the $m(H)$ curves $\approx 3$ nm agrees roughly with the TEM data. Comparison of the particle diameter and blocking temperature distribution suggests the important role of the surface anisotropy. The presence of an antiferromagnetic phase is indicated by the susceptibility $\chi_a$. Excepting the sample 1/900 the diameter of the nanoparticle increases with the annealing temperature and reaches $\approx 25$ nm at $T_{an}=1150^\circ$. For the $r=Co/Fe=1$ sample annealed at $900^\circ$ an anomalous form of the hysteresis loop was explained by the presence of single and multi-domain particles.
Figure 5. The hysteresis loops at T=15 K measured for the Co/Fe=1 samples

Figure 6. a) Form of the virgin curves at T=15 K, b) components of the hysteresis curve for the sample 1/900.

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