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The Role of Superparamagnetic Particle Size Distribution and Ferromagnetic Phase on GMR in Granular Cu-Co Alloys

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Relations between giant magnetoresistance (GMR) characteristic, magnetic properties and structure were investigated in $Cu_{90}Co_{10}$ alloy obtained by melt spinning in which GMR was enhanced by appropriate annealing. The structure of the annealed sample is not homogeneous (though the sizes distribution of the majority of Co-particles is not very wide but much larger particles are also present). On the other hand, the GMR characteristics differs from that expected theoretically for identical superparamagnetic particles. It is shown that ther main sources of the observed non-quadratic magnetoresistance dependence on magnetization are differentiated surface to volume ratio of superparamagnetic particles and the ferromagnetic phase contribution to the total magnetization which was calculated applying the new method.

1. Introduction

Following the discovery in antiferromagnetically coupled multilayered films [1], the giant magnetoresistance (GMR) effect has been observed in several types of magnetic nanostructures in which the relative orientation of magnetic entities can be changed by an applied field. It can be heterogeneous alloy systems in which small amounts of a magnetic material are well dispersed in a nonmagnetic, metallic matrix forming single domain magnetic regions, as for example heterogeneous thin films [2] or even granular alloys obtained by melt spinning [3]. The origin of GMR in these materials is the spin-dependent scattering which originates from the randomly aligned single domain regions. The resistivity has maximum when the misalignment is the largest. The effect is related to the size and volume density of the particles, as well as to the effective magnetization [4]. It is commonly accepted that the spin-dependent scattering of conduction electrons at the interfaces (between magnetic and nonmagnetic regions) play the essential role, while scattering within the magnetic particles seems to be less important [5].

When superparamagnetic particles are identical and possible interactions can be neglected, a quadratic dependence of the resistivity on magnetization (M) is theoretically expected [5, 6], however, significant deviation from this dependence for the experimental data has been reported [2, 7], the nature of which is not satisfactory interpreted yet.

In this work the magneto-transport properties and microstructure of isothermally annealed melt-spun Cu-Co alloy are studied. It is shown that observed non-quadratic dependence of the magnetoresistivity on magnetization arises from the size-distribution of superparamagnetic particles as well as from the presence of the ferromagnetic phase. The amount of ferromagnetic phase was calculated applying the new invented method (involving Fourier transform filtering and remanence coercivity measurement).

2. Experimental

Rapidly quenched $Cu_{90}C_{10}$ - ribbon, was annealed in vacuum at 500°C for 1 h. The microstructure of the sample (thinned down by ion etching) was inspected by the transmission electron microscopy (TEM). The magnetization histeresis loops were obtained using vibrating-sample magnetometer (MagLab 1.2T VSM, Oxford Instruments, Ltd) for the field up to 1.1 T. The magnetoresistance was measured by four-wire method (D.C. current I = 10 mA) in the magnetic field up to 0.8 T applied in the longitudinal or transverse configurations.

3. Results and Discussion

Observations of the annealed sample by TEM reveal a complex microstructure, composed mainly of small particles of the size of few nanometers as well as of the particles of the size even an order of magnitude larger. The complexity of the microstructure results also from the appearance of a distribution of both, particle sizes and inter-particle distances (agglomerations of small particles are also seen in TEM-micrographs). The particles themselves exhibit fcc-Co structure which is constrained by the Cu-matrix [8].

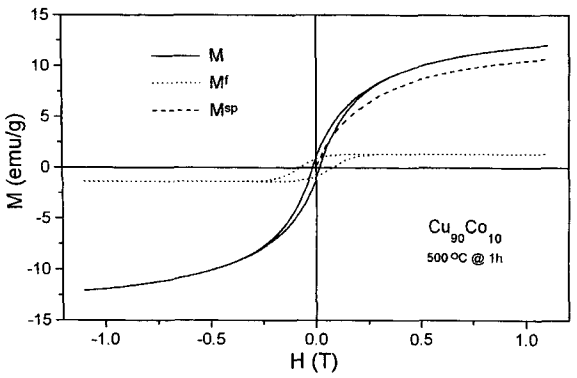

Fig. 1. Histeresis loop of the annealed $Cu_{90}Co_{10}$ sample and calculated ferromagnetic and superparamagnetic components of the magnetization.

The room temperature hysteresis loops of the sample (Fig. 1), are not saturated for the field up to 1.1 T, the feature characteristic of small superparamagnetic particles. However, as it is seen, the sample exhibits small coercivity (H_c) and remanence (M_r) which can be attributed to the presence of ferromagnetic phase, which can originate from the larger particles or from the agglomerations of the particles of much smaller sizes. Therefore, the total magnetization of the sample can be expressed

$$M(H) = M^{sp}(H) + M^{f}(H), \tag{1}$$

where: M^{sp} is the superparamagnetic particle contribution, wereas M^f describes the ferromagnetic contribution. A source of the coercivity can not be only the ferromagnetic particles of the size much larger than the critical one for superparamagnetic behavior (at room temperature) but also the particles with the size close to the critical one. Such particles should become superparamagnetic at higher temperatures. The hysteresis loops measured up to 300 °C show that the coercivity does not change practically with the temperature. This fact seems to confirm the presumption that the hysteresis originates mainly from the ferromagnetic phase (created by much larger particles or agglomerations of smaller ones) which is sufficiently stable against temperature.

A separation of superparamagnetic and ferromagnetic contributions can be made in various ways. It can be assumed, for example, that the saturation magnetization of the ferromagnetic phase equals $M_s^f = M_r/0.866$, similarly as for the disordered system of single-domain cubic particles [9]. However the above method as well as a number of similar approximations shown in the literature, is rather arbitrary.

In the present paper the ferromagnetic contribution is determined from the difference between two branches of the hysteresis loop $\Delta M(H) = M(H\downarrow) - M(H\uparrow)$, the method which allows to calculate exactly this contribution. Taking into account (1), one has

$$\Delta M(H) = M(H\downarrow) - M(H\uparrow) = M^f(H\downarrow) - M^f(H\uparrow) \tag{2}$$

since $M^{sp}(H\downarrow) = M^{sp}(H\uparrow)$. Assuming that $M^f(H\downarrow)$ and $M^f(H\uparrow)$ can be obtained by a shift of the same function $M_0^f(H)$, i.e.

$$M^f(H\downarrow) = M_0^f(H+H_c^f),\ M^f(H\uparrow) = M_0^f(H-H_c^f), \tag{3}$$

both branches of $M^f(H)$ can be determined from their difference, if only the coercive field of the ferromagnetic phase (H_c^f) is known (it should be noticed, that H_c^f is, in general, different from the coercive field H_c obtained from the hysteresis loop of the total magnetization).

In order to determine $M_0^f(H)$, the Fourier transform can be used, which is usually defined

$$F(\nu) = \Im\{f(x)\} = \int_{-\infty}^{\infty} f(x) e^{-i2\pi x\nu} dx. \tag{4}$$

In the case of non-integrable functions, the so called generalized Fourier transform should be used in theoretical considerations. It can easily be shown that the Fourier transform of the difference of the shifted functions $\Delta f(x) = f(x+x_0) - f(x-x_0)$ is equal

$$\begin{aligned}\Im\{\Delta f(x)\} &= \Im\{f(x+x_0) - f(x-x_0)\} \\ &= \Im\{f(x)\}(e^{i2\pi x_0\nu} - e^{-i2\pi x_0\nu}).\end{aligned} \tag{5}$$

Dividing the Fourier transform given above by the expression in the parentheses, i.e. $H(\nu) = \exp(i2\pi x_0\nu) - \exp(-i2\pi x_0\nu)$, and next calculating the inverse Fourier transform, the original function $f(x)$ can be recovered. The details of the method will be described elsewhere. In order to determine H_c^f, the dc demagnetization remanence $M_d(H)$ was measured (after saturation of the sample in one direction, a small field in opposite direction was applied, which were next reduced to zero). The remanence coercivity H_r obtained this way approximates H_c^f. The obtained ferromagnetic as well as superparamagnetic components, the latter calculated using (1), are shown in Fig. 1. As it is seen, H_c^f is much larger than H_c.

For a set of non-interacting superparamagnetic particles the magnetization process can be described by classical Langevin formula. Considering the distribution of the particle sizes, the field dependence of magnetisation of superparamagnetic particles is fitted by the weighted mean of Langevin functions

$$M^{sp}(H) = M^{sp}(\infty) \sum_j f(m_j) L(m_j H / k_B T), \tag{6}$$

where: m_j - magnetic moment of the particle, $f(m_j)$ - weighing factor and $L(x) = \coth(x) - (1/x)$. The sum of four components were used in the fitting procedure similarly as in [10]. The values of m_j obtained from the best fit were then used to calculate the particles diameters D_j (assuming their spherical shape and that the saturation magnetization equals to that of the bulk fcc-Co). The obtained size range 2-5 nm for superparamagnetic particles is in a good agreement with that observed in TEM - micrograph for smaller particles

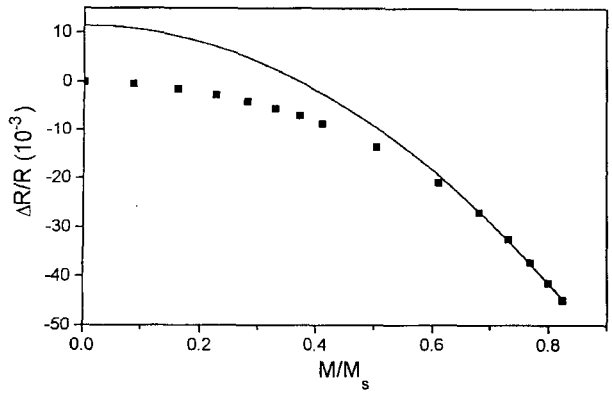

Fig. 2. Magnetoresistance characteristics and quadratic dependence fitted to the experimental points performed in higher magnetization range.

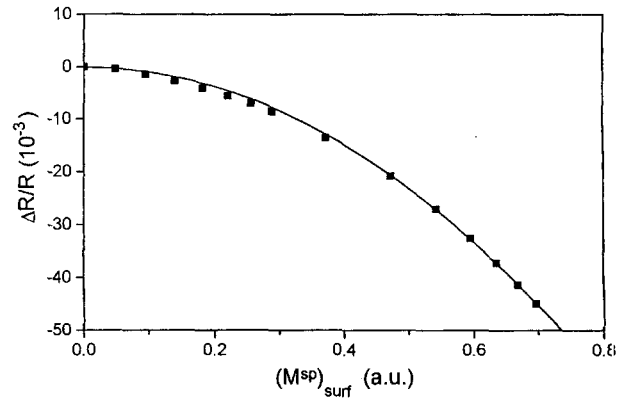

Fig. 3. Magnetoresistance versus "surface weighted magnetization". The solids line shows fitted quadratic dependence.

and is comparable with those reported in the literature. Saturation magnetization of the sample calculated as $M_s = M_{sp}(\infty)+M_s^f$ gives only 9% of the magnetization of bulk fcc-Co showing that the sample contains about 9% of Co-crystalline phase. About 10% of the total volume of this phase constitutes ferromagnetic particles.

The measured dependence of the resistivity on the magnetization is shown in Fig. 2, where the relative magnetoresistance ratio $(\Delta\rho/\rho)$ is defined as $[R(H)-R(0)]/R(0)$. In this figure, $(\Delta\rho/\rho)$ values are the average of the values obtained for the longitudinal and transverse effects (a few percent difference between both effects was observed, reflecting a conventional anisotropic magnetoresistance phenomena). Magnetoresistance does not saturate in the maximum applied field. The solid curve represents the fit to the parabolic dependence performed for larger magnetization values. The experimental data for low magnetization range are lying far from the parabolic curve. Plotting the same set of data versus magnetization of superparamagnetic particles ony, the deviation from parabolic curve becomes smaller since only superparamagnetic particles contribute to GMR. However, the effect of "flattening" is still significant.

Because the scattering at the interfaces of Co-particles is the main source of GMR effect, consequently smaller particles have greater relative contribution to GMR than to the magnetization of the sample [5, 11]. Therefore, the dependence of $\Delta\rho/\rho$ on M^{sp} in the real material should be different from that for the identical particles, since small particles saturate slower than the large ones (in agreement with the m_jH term in the argument of the Langevin function). An auxiliary quantity, termed the "surface weighted magnetization", were introduced in order to take into account the differentiated surface to volume ratio of the particles

$$(M^{sp})_{surf}=const\sum_j (1/D_j)f(m_j)L(m_jH/k_BT), \qquad (7)$$

where D_j - the particle diameter and $f(m_j)$ - the weighing factor obtained in the course of the fitting of $M^{sp}(H)$ to equation (6) (it should be stressed out that the introduced quantity $(M_{sp})_{surf}$ has no relations with the commonly known term "surface magnetization"). The relative resistivity $\Delta\rho/\rho$ plotted as a function of $(M^{sp})_{surf}$ should be similar in its shape to the hypothetical dependence of $\Delta\rho/\rho$ on M^{sp} for identical particles. Such a plot, obtained for the sample studied, is shown in Fig. 3 ($\Delta\rho/\rho$ data are the same as those in Fig. 2). In the coordinates in which the differences in the surface to volume ratio are compensated, the experimental results are well approximated by the quadratic dependence (solid line). This result shows the importance of both, the particle size distribution and the presence of ferromagnetic phase while analyzing GMR in granular materials.

The values of "surface weighted magnetization" $(M^{sp})_{surf}$ (the quantity which is a function of the magnetic field) were calculated using fixed m_j, $f(m_j)$ and D_j parameters only. They were obtained from the earlier analysis of the $M^{sp}(H)$ - dependence. The quantity $(M^{sp})_{surf}$ may be normalized in such a way, that it will have the same dimension as the magnetization M (i.e. magnetic moment per unit volume). Thus, it can be interpreted as the weighted mean magnetization with respect to the surface of the particles. The plot of GMR vs. $(M^{sp})_{surf}$ is a useful method to test the role of the differences in the surface to volume ratio of the particles prior to the invention of more sophisticated models. The method is universal since it is not restricted to one theoretical model only and to the specific type of the particle size distribution

4. Conclusions

Granular magnetic material obtained by the annealing of $Cu_{90}Co_{10}$ melt-spun ribbon is inhomogeneous in respect of the Co-particle sizes and distances between particles. For that reason not all particles demonstrate superparamagnetic behavior. The original method allowing exact calculation of the ferromagnetic contribution to the total magnetization is invented. This contribution and the differentiated surface to volume ratio of the superparamagnetic Co-particles are considered as two sources of the observed deviation of the experimental dependence of GMR on magnetization from

that expected theoretically. Data analysis were performed using a new method, which consider introduced the "surface weighted magnetization". Satisfactory agreement between experimental and calculated dependencies was achieved taking into account real properties of the material deduced from the magnetic as well as from the structural characteristics.

Acknowledgments

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