Journal of Magnetics 4(3), 76-79 (1999)

Glassy Dynamics in Giant Magnetoresistive Melt-spun Co-Cu

B. Idzikowski[1,2], U. K. Rößler[1], A. Handstein[1], D. Eckert[1], M. Wolf[1], K. Nenkov[1,†] and K.-H. Müller[1]

[1]*Institut für Festköper- und Werkstofforschung Dresden, P.O. Box 270016, 01171 Dresden, Germany*
[2]*Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland*

(Received June 5, 1999)

We report results on metastable CuCo ribbons at low Co contents (2 and 10 at%), which were prepared by conventional melt-spinning technique and subsequent annealing. The properties of these materials cannot consistently be described by those of an assembly of superparamagnetic single-domain particles. Magnetic measurements related to magnetic dynamics reveal spin-glass-like properties. Especially, we find very slow non-equilibrium relaxation processes in $Co_{10}Cu_{90}$, which depend on prehistory, when probing the relaxation of the resistivity. The results are clear evidence for frustrated interaction effects due to magnetic couplings between Co clusters or precipitates in these alloys.

1. Introduction

Giant magnetoresistance (GMR) in granular alloys containing very fine ferromagnetic particles in a metallic matrix relies on the spin-dependent scattering at or in different magnetic entities [1, 2]. Melt-spun Co-Cu ribbons show this effect [3, 4]. The microstructure responsible for the GMR is produced by partial decomposition of this immiscible alloy system. This microstructure consists of nano-sized spherical Co precipitates in a Cu matrix, which is depleted of residual Co atoms. However, the details of the relation between microstructure and the GMR behavior are not yet understood. From magnetic data, cluster sizes can be determined provided that the system behaves as an assembly of superparamagnetic particles [5]. Thus, one assumes the particles are single-domain ferromagnetic and independent of each other. Here, we report on a series of measurements which are aimed at testing the magnetic behaviour of Co_2Cu_{98} and $Co_{10}Cu_{90}$ melt-spun and annealed ribbons. We will first try to interpret our data on a set of samples of $Co_{10}Cu_{90}$ by the assumption of superparamagnetic behaviour. Then, we will point out some deficiencies of this interpretation. And, we will provide evidence of collective frustrated behaviour due to magnetic couplings between the Co precipitates in these materials.

2. Experimental

CoCu ribbons were prepared by melt spinning on a Cu wheel and subsequently heat treated. Details of the preparation procedure are described in Ref. [4]. The temperature and field dependence of magnetization were measured using a SQUID magnetometer and vibrating sample magnetometers. The ac-susceptibility of χ was measured in a commercial susceptometer. The electrical resistance was measured by the dc four-probe technique.

3. Results and Discussion

3.1. Superparamagnetism

Table 1 lists results of magnetoresistance measurements for a series of $Co_{10}Cu_{90}$ samples, which were annealed at $T_a = 500$ °C for various times up to several days. The magnetotransport behaviour is characterized by the magnetoresistance ratio $MR = (R(H;T) - R(0;T))/R(0;T)$, where $R(H;T)$ is the resistance at an applied magnetic field H and at a temperature T. The magnetoresistance ratios MR given in Table 1 were measured at a temperature of 10 K in a field of 5 T. They are drastically increased by short-time annealing compared to the as quenched (a.q.) state. But, the magnetoresistance ratios drop with annealing time τ_a. We have measured the initial susceptibility χ for this set of samples. In Fig. 1 the inverse susceptibilities $1/\chi(T)$ are plotted against temperature. Using the temperature dependence of the susceptibilities, two routes to estimate the sizes of the Co clusters can be applied, which are both based on the superparamagnetic model. For the first, the data are fitted to a Curie-Weiss law $\chi(T) = C/(T-\theta)$ and cluster-sizes are calculated from the Curie constant C. The other method uses the minima of the $1/\chi\ (T)$ curves, which are interpreted as superparamagnetic blocking induced by the anisotropies of the Co clusters. The results in Fig. 1 show that the blocking

[†]On leave from International Laboratory of High Magnetic Fields, Wrocław, Poland, and ISSP, Bulgarian Academy of Science, Sofia, Bulgaria.

Table 1. $Co_{10}Cu_{90}$ ribbons annealed for different times τ_a at 500 °C. Results for magnetoresistance ratio MR at a temperature of 10~K in field of 5 T and estimates for Co particle sizes. The estimated average or typical diameters are $<D^C>$ from Curie-Weiss law with Curie constant C. μ_{eff} and N are the corresponding average moments and numbers of Co atoms, respectively. Diameters $<D^{TB}>$ are estimates from blocking temperatures T_B. For short-time annealed samples two blocking temperatures are considered (see text for further explanations)

τ_a [min]	MR (10 K, 5 T) [%]	C [$10^7 \frac{emuK}{Oemol}$]	μ_{eff} [mB]	N	$<D^C>$ [nm]	T_B [K]	$<D^{TB}>$ [nm]
a.q.	-12.3	1.07	610	350	2.0	TB1 ≃ 17	3.7
						TB2 ≃ 190	8.2
2	-29.7	1.62	925	530	2.2	TB1 ≃ 17	3.7
						TB2 ≃ 190	8.2
20	-24.0	1.85	1060	605	2.3	18.5	3.8
200	-16.3	2.68	1540	880	2.6	27	4.3
2000	-7.4	19.4	11100	6340	5.2	107	6.4
8000	-4.2	–	–	–	–	–	–

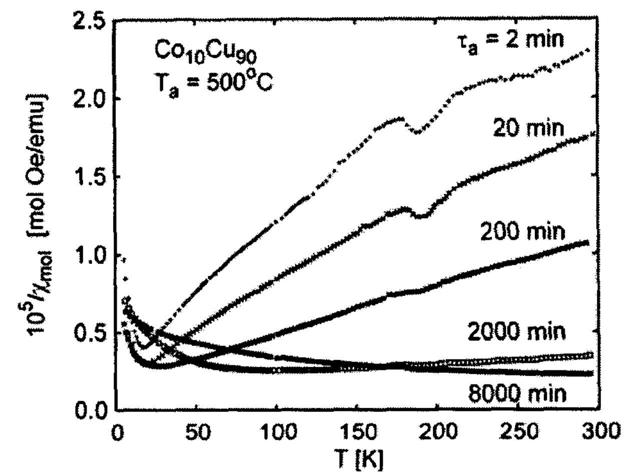

Fig. 1. Inverse molar susceptibility versus temperature of $Co_{10}Cu_{90}$ ribbons annealed at $T_a = 500$ °C for different times

temperature T_{B1}, i.e. the minimum of $1/\chi(T)$, shifts to higher temperature for longer anneals. This can be ascribed to growth and coarsening of the Co precipitates. There are further local minima at a temperature T_{B2} of about 190 K in as-quenched samples (not shown here for clarity) and in short time ($\tau_a \leq 200$ min) annealed samples. We assume that these minima signal the presence of fcc-Co particles which are heterogeneously nucleated in grain-boundaries during the rapid quenching. Such particles in grain-boundaries have been observed recently by field-ion microscopy on melt-spun $Co_{10}Cu_{90}$ [6].

It is readily seen that a Curie-Weiss law is only approximately valid for our short time annealed samples because $1/\chi(T)$ is not linear above the first blocking temperature T_{B1}. Nonetheless, to derive rough estimates, we fitted our $1/\chi$ data with a Curie-Weiss law. The Curie constants C are given in Table 1. The corresponding effective moments μ_{eff}, *numbers of atoms* N of the average Co clusters, and diameters $<D^C>$ are also given. The sizes of the clusters were calculated from their effective moments by assuming a contribution of 1.753 μ_B per Co atom as in bulk fcc-Co. The values of the "paramagnetic Curie temperature" θ are negative here, which may be seen as an indication for interaction effects with anti-ferromagnetic bias.

The other route to estimate fine-particle sizes is based on anisotropies of the particles. The mean volume $<V>$ can be derived from the relation $\ln(\tau/\tau_0)$, k_B, $T_B = K<V>$, where the effective anisotropy constant K must be known. For static measurements we use a time-factor $\ln(\tau/\tau_0) \simeq 30$ with a characteristic time-constant $\tau_0 \sim 10^{-9} \cdots 10^{-11}$ s. When using an estimate for $K = 2.7\times10^6$ erg/cm^3 [7] we can derive the diameters $<D^{TB}>$ in the last column of Table 1. The values are systematically larger than those from Curie-Weiss law. Moreover, recent measurements on fcc-Co films at room temperature indicate smaller intrinsic, magnetocrystalline anisotropies of the order of K~5×10^5 erg/cm^3 [8]. This would lead to even larger differences between $<D^{TB}>$ and $<D^C>$. Therefore, one usually assumes that fine-particles own much higher anisotropies of the order of $10^{7\cdots8}$ erg/cm^3, e.g. due to surface contributions and other effects [9, 10].

One sample annealed for $\tau_a = 20$ min at $T_a = 500$ °C was studied in more detail. Measurements of demagnetization curves are shown in Fig. 2. These data taken above the apparent blocking temperature were fitted using a superposition of Langevin-functions to describe a distribution of spherical particles with diameters D. We take a linear-log-normal distribution $f(D)$ to this end. The temperature dependent saturation magnetization $M_{sat}(T)$ of bulk Co-fcc is used to get the magnetic moments of the particles $M_{sat}\pi D^3/6$. From the fit, we find a median diameter of 2.1 nm. This is in fair agreement with the value $<D^C> = 2.3$ nm from the Curie-Weiss law. In Fig. 3 thermomagnetic curves for the same sample are shown. Field-cooled (FC) and zero-field-cooled (ZFC) curves were measured during reheating. The bifurcation between the two curves starts close to room-temperature. Thus, there should be a significant amount of blocked particles on timescales of 100 s at 300 K. Using

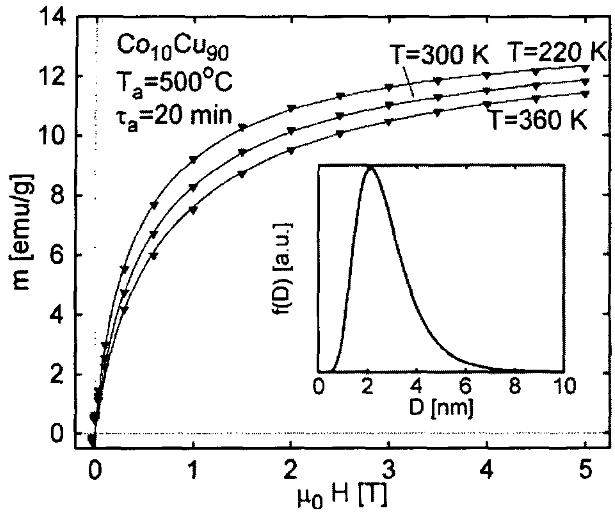

Fig. 2. Magnetization versus applied field at three high temperatures for an annealed $Co_{10}Cu_{90}$ sample. The full lines are fits to the data using a superposition of Langevin-functions with a distribution $f(D)$ of particles with diameters D. The distribution, which was obtained by fitting all data with one single distribution, is plotted in the inset.

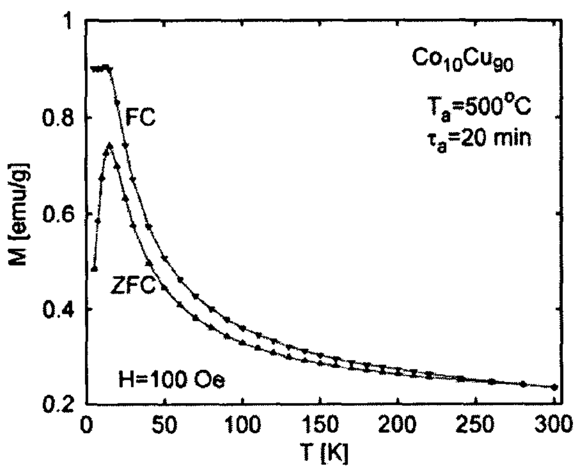

Fig. 3. Thermomagnetic curves for the same sample as in Fig. 2. Measurement in a field of $H = 100$ Oe by field-cooling (FC) and zero-field-cooling (ZFC).

$K = 2.7{\times}10^6$ erg cm^{-3}, we find that these particles should have $D > 9$ nm. In the distribution used for the Langevin-fit (Fig. 2), no significant amount of such particles is present. Again, larger values of K would result in lower estimates for the diameters of blocked particles at room-temperature. With $K \sim 10^7$ erg cm^{-3}, we would get $D \sim 6$ nm. However, such enhanced anisotropies for relatively large particles are unexpected. There is no obvious mechanism to explain this strong increase of anisotropy. The same conclusion can be reached from the relaxation of field-cooled magnetizations measured for the same sample at low temperatures (Fig. 4). There is a logarithmically slow decay on timescales of 100 min after cutting the field. Particles relaxing on such long timescales should have diameters D around 4 nm, if we put the anisotropy constant to $K =$

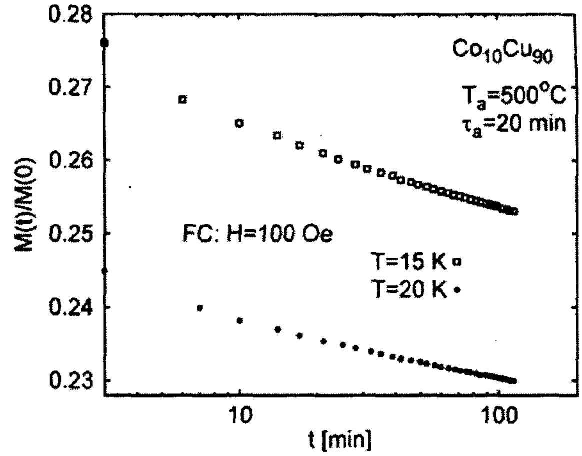

Fig. 4. Relaxation of the remanence for the same sample as in Fig. 3 after field-cooling in $H = 100$ Oe. At time $t = 0$ the field is cut. Magnetization is normalized to the magnetization, which was measured at this time with applied field.

$2.7{\times}10^6$ erg cm^{-3}.

3.2. Spin-glass-properties

In a recent study [11], we showed from ac-susceptibility measurements that the Co precipitates in granular Co_2Cu_{98} are magnetically coupled and that the apparent superparamagnetic blocking is in reality a spin-glass-like collective freezing. The relation between timescale $\tau = 1/\omega$ and peak temperature T_p, where the ac-susceptibility $\chi(T;\ \omega)$ has its maximum, can be described by a critical dynamical law $\tau = \tau_0\ ((T{-}T_c)/T_c)^{-z\nu}$ [12]. The corresponding fits are shown in Fig. 5. The parameters used were the following $T_c = 33{\pm}2$ K ($11{\pm}2$ K, $4{\pm}1$ K) with $z\nu = 6.5{\pm}1.25$ ($9.5{\pm}2.0$, $9.0{\pm}3.0$)) for samples annealed for $\tau_a = 180$ min (60 min, 7 min), respectively. The microscopic timescale must be set

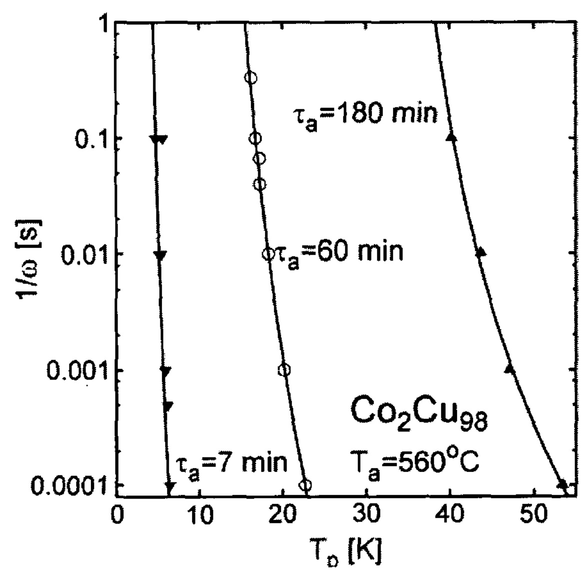

Fig. 5. Dynamic critical scaling for Co_2Cu_{98} samples. Inverse measuring frequency $1/\omega$ is plotted versus temperature T_p of the corresponding peak of χ $(T;\ \omega)$. Lines are fitted critical law $1/\omega = \tau_0\ ((T{-}T_c)/T_c)^{-z\nu}$.

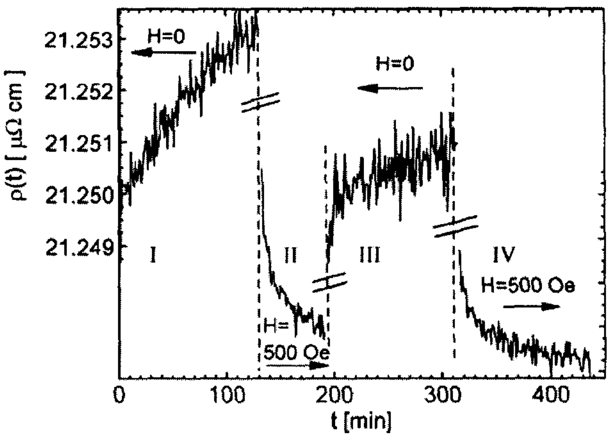

Fig. 6. Relaxation of the resistivity of a $Co_{10}Cu_{90}$ sample. Time $t = 0$ starts after zero-field-cooling to $T = 5$ K when temperature is stable (time interval I). During the intervals II and IV, a field $H = 500$ Oe is applied, which is switched off in interval III. The response of the resistivity depends on the accumulated prehistory.

in the range $\log_{10}(\tau_0/s) = -5\pm1$ for these fits. Thus, even in dilute systems the dynamics clearly indicates the presence of frustrated interaction between magnetic units in granular CuCo.

We have found similar but stronger features of spin-glass behaviour in $Co_{10}Cu_{90}$ samples. This includes very slow relaxation phenomena and dependence on prehistory found in time-dependent measurements. This signals the non-stationary dynamics which is reached by cooling when the collective magnetic system falls out of equilibrium and relaxes on very long time-scales. In these granular metals, this can be studied simply by time-dependent measurements of the resistivity response to changes of temperature and field. In Fig. 6, an example for this complex behaviour is shown.

4. Conclusions

There are some subtle short-comings with the superparamagnetic model for the magnetism of relatively dilute granular CuCo-alloys. By measuring dynamic properties, we find that the apparent blocking is rather a spin-glass-like collective freezing transition. This is an explanation for the discrepancies we have found, when comparing estimates for particle sizes in these systems gained by different methods. Estimates based on a Curie-Weiss law consider interactions by a mean-field approximation. On the other hand, estimates from an apparent blocking temperature ascribe interaction effects to an enhanced anisotropy of particles, which is not correct. Thus, these two ways of describing the magnetic behaviour of the granular system may yield largely different results. One may speculate, that the superposition of Langevin-functions to describe high temperature magnetization curves could yield the best simple estimates. However, glassiness is visible in these systems from the difference between field-cooled and zero-field-cooled thermomagnetic curves up to room-temperature. Thus, the description by freely rotating superparamagnetic particles is not valid also at room temperature, and any estimates for particle sizes based on this method will be systematically in error because of these interaction effects. Glassy dynamics due to (frustrated) magnetic couplings between magnetic units also explains the slow relaxational dynamics found for these granular metals. Thus, interaction effects must be studied for a deeper understanding of magnetic and magnetotransport properties of granular metals.

Acknowledgment

B. I. was supported by Saxonian Ministry for Sciences and Arts. Part of the work was supported by SFB 422.

References

[1] A. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett., **68**, 3745 (1992).
[2] J. Q. Xiao, J. S. Jiang, and C. L. Chien, Phys. Rev. Lett., **68**, 3749 (1992).
[3] J. Wecker, R. von Helmholt, L. Schultz, K. Samwer, Appl. Phys. Lett., **62**, 1985 (1993).
[4] B. Idzikowski, K. Nenkov, A. Handstein, A. Hütten, and K.-H. Müller, Acta Phys. Pol., **A 92**, 307 (1997).
[5] I. S. Jacobs and C. P. Bean, Magnetism, eds. G. T. Rado, H. Suhl, Acad. Press, vol. III, 271 (1963).
[6] R. Busch, F. Gärtner, C. Borchers, P. Haasen and R. Bormann, Acta mater., **44**, 2567 (1996).
[7] R. H. Yu, X. X. Zhang, J. Tejada, M. Knobel, P. Tiberto, and P. Allia, J. Appl. Phys., **78**, 392 (1995).
[8] D. Weller, G. R. Harp, R. F. C. Farrow, A. Cebollada, and J. Sticht, Phys. Rev. Lett., **72**, 2097 (1994).
[9] C. L. Chien in Science and Technology of Nanostructured Magnetic Materials, eds. G. C. Hadjipanayis and G. A. Prinz, Plenum Press, New York 1991, p. 477.
[10] B. J. Hickey, M. A. Howson, D. Greig, and N. Wiser, Phys. Rev., **B 53**, 32 (1996).
[11] B. Idzikowski, U. K. Rößler, D. Eckert, K. Nenkov, K.-H. Müller, Europhys. Lett., **45**, 714 (1999).
[12] J. Souletie and J. L. Tholence, Phys. Rev., **B 32**, 516 (1985).