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Asymmetric giant magnetoresistance in $Co_{10}Cu_{90}$ magnetic granular alloys

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We have observed a type of giant magnetoresistance (GMR) in magnetic granular $Co_{10}Cu_{90}$ alloys. The asymmetric GMR depends strongly on the size of magnetic Co particles, which exhibit superparamagnetic behavior at given measured temperature. The asymmetric GMR points to a metastable state that develops when the sample is field-cooled, which is lost after recycling. We propose that high-field cooling produces more effective parallel alignment of small unblocked Co particle moments and interfacial magnetizations, which contributes to the further decrease of the resistance in comparison with the samples zero-field-cooled, and then applied to the same field.

Two groups[1,2] have reported that the giant magnetoresistance (GMR) can be also achieved in heterogeneous alloys, in which magnetic single-domain clusters are embedded in a nonmagnetic metallic matrix. Since these pioneering works, there has been a growing interest in the study of GMR effect in magnetic granular materials.[3–10] The resistance is high for the random alignment of magnetic cluster moments, and it is decreased substantially when individual moments are aligned parallel by an external magnetic field. It is now widely accepted that the GMR effect is associated with the reorientation of the magnetic cluster moments and has been interpreted on the basis of electron spin-dependent scattering occurring in the magnetic clusters as well as at the magnetic and nonmagnetic interfaces,[11,12] and the interfacial spin-dependent scattering plays the dominant role.[13]

Co and Cu elements are nearly immiscible, and no equilibrium phases exist in the Co-Cu binary phase diagrams. However, the high cooling rate during sample preparation may result in metastable CoCu alloys with extended solubility. More recently, rapid solidification (melt-spinning) has been shown to be a suitable method for preparing bulk GMR CoCu granular alloys.[14–17]

In this paper we present magnetization and GMR results on $Co_{10}Cu_{90}$ magnetic granular alloys, prepared by melt-spinning and subsequent heat treatment. We observe the appearance of a type of GMR, which is a consequence of high field-cooled (FC) process.

Homogeneous metastable $Co_{10}Cu_{90}$ alloys have been prepared by melt-spinning technique. The spun ribbons (length 0.1 m, width 0.05 m, thickness 6.0×10^{-5} m) were obtained by planar flow-casting in a controlled atmosphere on a CuZr drum. The as-quenched samples were annealed at elevated temperatures T_A in the range 350–600 °C for 30 min in a vacuum of 1.5×10^{-5} Torr in order to allow the formation of the magnetic granular CoCu alloys consisting of single-domain ferromagnetic Co clusters embedded in the nonmagnetic Cu matrix. The samples were routinely subjected to x-ray diffraction (XRD) and differential scanning calorimetry (DSC) characterization. The magnetoresistance was measured using direct current four-terminal geometry attached to a superconducting quantum interference device (SQUID) magnetometer in a magnetic field up to 50 kOe with a temperature change from 4.2 to 320 K.

Owing to the coherency of the Co and Cu lattices, x-ray diffraction is ineffective for investigating very small Co clusters in CoCu samples annealed at temperatures below 550 °C, where diffraction lines corresponding to fcc Co particles start to appear at d spacing. On the other hand, DSC is a technique which is sensitive to the Co particle precipitation process during thermal annealing.[18] The Co phase separation starts at a temperature of about 350 °C, and finishes at $T\approx$ 700 °C. The calculated exothermic heat release during Co phase separation is lower than the heat of mixing for a CoCu alloy with the same composition obtained by the thermodynamic calculation. This result indicates that some Co particles have been already formed during rapid solidification from the melt state.

Figure 1 shows the magnetization curves measured at 10

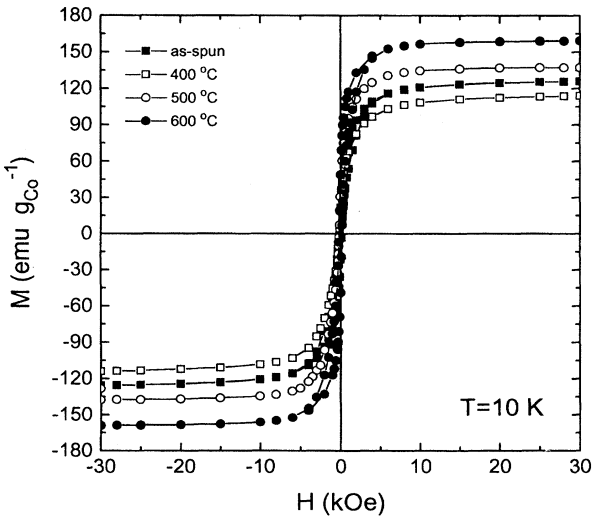

FIG. 1. The magnetization curves for representative samples measured at 10 K.

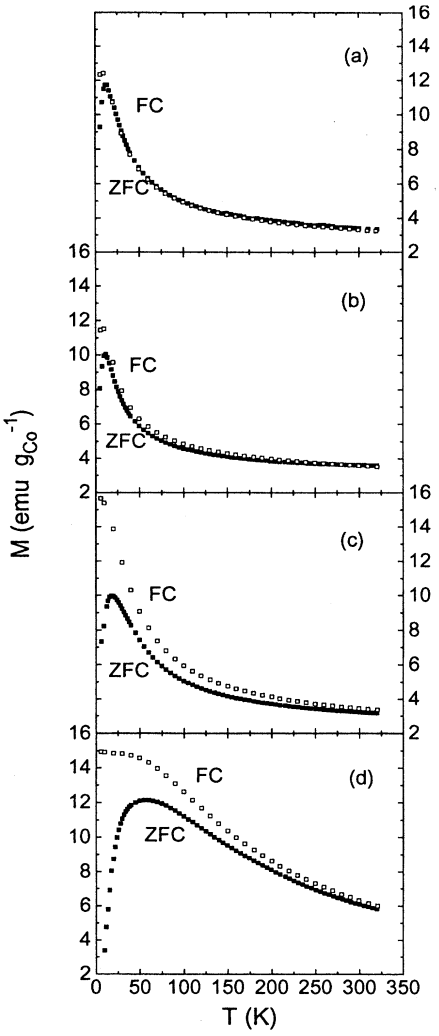

FIG. 2. Magnetization in a field of 50 Oe for selected samples both in field-cooled (FC) and zero-field-cooled (ZFC) states. (a) as-quenched, (b) T_A = 350 °C, (c) T_A=500 °C, and (d) T_A=600 °C.

K. We found that the saturation magnetization M_s primarily decreases with increasing annealing temperature and reaches the minimum value of 115.0 emu g_{Co}^{-1} at T_A=400 °C, then increases to the value of 158.0 emu g_{Co}^{-1}, which is slightly lower than the M_s value of 175.0 emu g_{Co}^{-1} for the bulk fcc Co.[19] The same change tendency with annealing temperature has been also observed for the magnetization of the samples in both field-cooled (FC) and zero-field-cooled (ZFC) states in an applied field of 50 Oe (Fig. 2). In the as-quenched state, the ZFC magnetization peak temperature T_p is about 12.0 K, and it slightly decreases until T_A = 400 °C, then increases as T_A is increased. Apparently, the change of magnetization with annealing temperature is related to the Co particle precipitation process. We assume that some Co-rich regions were formed during rapid solidification, and at an early stage of phase separation during thermal annealing, the formation of fine superparamagnetic Co clusters would reduce the saturation magnetization M_s and ZFC magnetization peak temperature T_p. As T_A is further increased, the successive

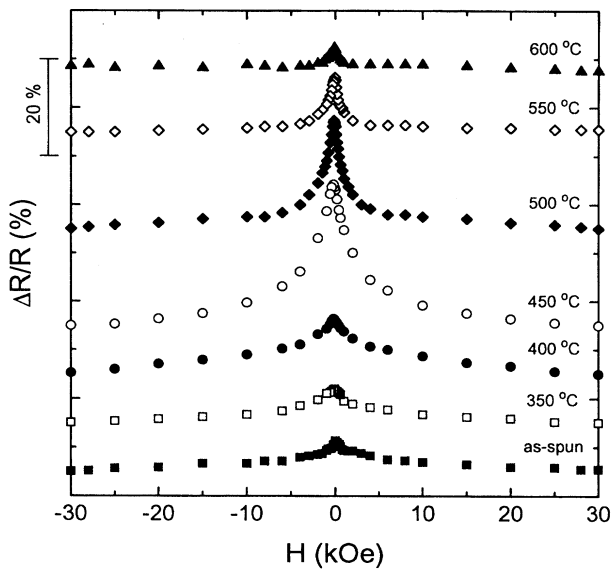

FIG. 3. $\Delta R/R$ versus H for the granular $Co_{10}Cu_{90}$ samples zero-field-cooled and measured at 10 K.

nucleation and growth of Co particles will increase the M_s and T_p as shown in Figs. 1 and 2. However, a clear description of phase separation and Co particle size and their relation with the magnetic data need a further detailed microstructural investigation.

As shown in Fig. 2 and previous works,[1,4,15] a large thermal hysteresis is observed for the annealed samples below a characteristic freezing temperature, where ZFC and FC curves diverge. The observation of thermal hysteresis much above the peak of ZFC curves indicates the existence of a broad distribution in the size and shape of the Co particles. Thus, a range of corresponding blocking temperatures will exist. Therefore, the thermally annealed samples behave as a mixture of superparamagnetic and cluster-glass, even ferromagnetic behaviors depending on T_A and compositions.

We now focus on the GMR and magnetization data for the samples zero-field-cooled and field-cooled to 10 K, then measured at this temperature. Figure 3 shows the GMR values as a function of the magnetic field for as-quenched and annealed samples zero-field-cooled and measured at 10 K. The normalized magnetoresistance $\Delta R/R$ is given by the usual definition,

$$\Delta R/R = \frac{R(H) - R(H_{\max})}{R(H_{\max})}, \tag{1}$$

where $H_{\max}$ is the maximum applied magnetic field. GMR was found to depend strongly on the annealing temperature T_A; it initially increases with increasing T_A, reaching the peak value of 33.0%, and then it decreases to a value of 5.0% at T_A=600 °C. A magnetoresistance (MR) change of 7.0% has been observed for the as-quenched $Co_{10}Cu_{90}$ ribbon at 10 K in the magnetic field of 30 kOe. This result is supportive of the previous assumption that some Co particles have been already formed during rapid solidification. For the samples in the as-quenched state or annealed at $T_A \leq 450$ °C, $\Delta R/R$ is not saturated by the field of 30 kOe,

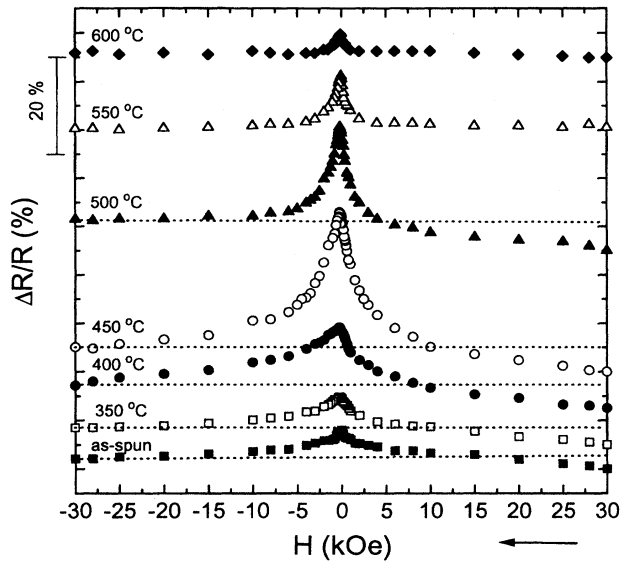

FIG. 4. $\Delta R/R$ versus H for the granular $Co_{10}Cu_{90}$ samples field-cooled in the filed of 30 kOe and measured at 10 K. The arrow indicates the applied field's change of direction.

otherwise, the samples annealed at $T_A \geqslant 500$ °C saturate relative quickly. In comparison with the magnetization data, the $\Delta R/R$ is more difficult to be saturated, especially for the samples as-quenched or annealed at low temperatures.

The field dependence of the MR for the samples field-cooled and measured at 10 K is shown in Fig. 4. The samples were applied to a field of 30 kOe at room temperature and cooled to 10 K, then the applied field was gradually changed in the opposite direction, at the same time the MR value was recorded. In comparison with zero-field-cooled samples, immediately it is apparent that the field dependence of MR for field-cooled samples shows an asymmetric behavior, but it disappears for the samples annealed at $T_A \geqslant 550$ °C. Figure 5 compares the MR for the sample annealed at $T_A = 450$ °C with its magnetization for the field applied parallel to the ribbon surfaces. The asymmetric GMR occurs when the applied field is changed from 30 kOe to -30 kOe, but the asymmetric behavior is lost when the magnetic field is changed in the opposite direction through zero, i.e., from -30 kOe to 30 kOe. Thus, it points to a metastable state that develops when the sample is field cooled, but which is lost, when at low temperature ($T = 10$ K), the field is swept through zero. At 4.2 K, a similar phenomenon in the initial state resistivity of Ag/Co magnetic layers has been observed by Pratt *et al.*[20] They found that the initial MR of their samples at $H = 0$ were larger than that the stablized MR at $M \approx 0$. In other words the zero-field-cooled state is also metastable, and it is lost when the field is swept through zero. Following Johnson,[21] they assumed that at H_M [the total resistance for the current perpendicular to the planes of the layers (CCP-MR) is maximum after cycling through the saturation field H_s for MR], the magnetization M_i of the neighboring ferromagnetic layers are oriented randomly in the layer plane, and that at $H = 0$ (the samples are zero-field-cooled) the ordering is nearly (but probably not completely) antiparallel along a single axis.[22] As shown in Fig. 5(b), the

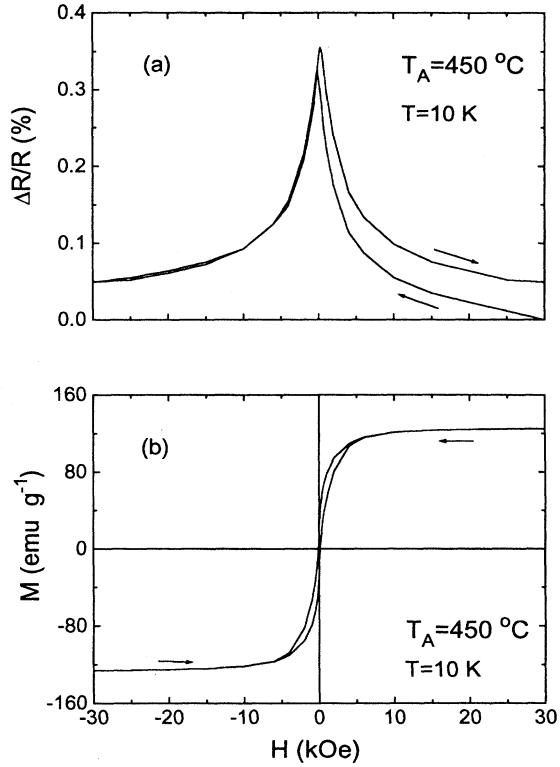

FIG. 5. (a) Magnetoresistance vs applied field measured at 10 K. (b) Magnetization curve for the same sample in the same experimental condition. The arrow indicates the applied field's change of direction.

asymmetric behavior shows up in the resistivity, but not in the magnetization curves. Therefore, we assume that the asymmetric MR comes from more effective parallel alignment of magnetizations of superparamagnetic entities in the high field-cooled samples than that in the samples zero-field-cooled, and then applied to the same field.

The field dependence of magnetoresistance, which is found to follow a quadratic dependence on the average magnetization of the alloys, as predicted for single-domain ferromagnetic particles in a nonmagnetic matrix,[11]

$$R(H) = \frac{\rho(H) - \rho(H_S)}{\rho(H_S)} = \frac{\rho_2^2}{\rho_1^2 - \rho_2^2}[1 - \alpha^2(H)] = A[1 - \alpha^2(H)]. \quad (2)$$

$R(H) = \Delta\rho/\rho$ is maximum for $H = H_c$ and $\alpha = M(H)/M_s = 0$. The key structural parameters influencing factor A, i.e., the GMR effect in granular systems, are the size of magnetic particles and the magnetic and nonmagnetic interface roughness. The GMR is widely accepted to be due to spin-dependent electron scattering in the magnetic particles as well as at the interfaces of magnetic and nonmagnetic entities. The crucial factor for GMR is $\langle \cos\varphi_{ij} \rangle$, where φ is the angle between the axes of the ferromagnetic clusters. If all the particles are assumed to have the same magnetic moments without correlation, one can obtain that

$\langle\cos\varphi_{i,j}\rangle=\langle\cos\theta\rangle$,[2] where θ is the angle between the magnetization axis of a particle and external field, and $\langle\cos\theta\rangle$ is averaged over many ferromagnetic particles.[2] As discussed above, the present alloys contain Co particles with a range of sizes; then there will be a corresponding range of blocking temperatures. Therefore, at a given low temperature, only a fraction of Co particles will be blocked, while the remainder will not be blocked. When the magnetic field is applied, the larger blocked Co particles align first they make a large contribution to the magnetoresistance since they are effective spin-dependent scatterers. As shown in Fig. 3 and in the previous works,[2,8] the magnetoresistance continues to decrease well above the applied field at which the larger clusters are saturated, producing a long tail to the magnetoresistance curves. This long tail may correspond with the slow approach to the saturation of the small unblocked clusters at given temperatures. Another structural factor that may be influencing the magnetization and GMR effect in granular systems is the interface roughness. Barlett *et al.*[8] have interpreted that the Langevin-like GMR they found depends on the magnetism of the interfaces of Co and Cu layers. In fact, the interface magnetism and the exchange interaction between the interface spins and the ferromagnetic Co spins at low temperature would certainly affect the magnetization and GMR configuration. Thus, it is likely assumed that the asymmetric GMR is associated with a more effective parallel alignment of small unblocked Co particle moments and interfacial magnetizations imprinted by the cooling in a field than that induced by applying the same field to the zero-field-cooled samples, which contributes to the decrease of resistivity, but it does not apparently increase the magnetization for $H=30$ kOe in comparison with zero-field-cooled samples. The alignment of small Co particle moments and interfacial magnetizations, and the asymmetric GMR caused by field-cooling, are metastable. They point to a metastable state that develops when the sample is field-cooled, but which is lost after recycling [Fig. 5(a)]. For the samples annealed at $T_A \geqslant 550\,^{\circ}\mathrm{C}$, the Co particles become larger and blocked at temperature much above 10 K, and also the interfaces may become sharper, therefore, the asymmetric GMR does not appear.

In summary we have demonstrated an asymmetric GMR which we believe is mainly the consequence of the more effective parallel alignment of small unblocked Co particle moments and interfacial magnetizations that was imprinted by the field-cooling. The asymmetric GMR strongly depends on the annealing temperature, i.e., the sizes and shape of the Co particles and interfacial sharpness. This asymmetric GMR effect is metastable, and it is lost after recycling.

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