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Magnetic properties and giant magnetoresistance of magnetic granular Co$_{10}$Cu$_{90}$ alloys obtained by direct-current joule heating

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The direct-current (dc) joule heating technique was exploited to fabricate giant magnetoresistance (GMR) Co$_{10}$Cu$_{90}$ granular alloys. The Co cluster precipitation process was investigated by calorimetric and x-ray diffraction measurements. At $T=10$ K, the largest MR change of 25.0% has been observed for the melt-spun Co$_{10}$Cu$_{90}$ ribbon annealed at $I=5$ A. The magnetoresistance scales approximately as the inverse Co particle size. At room temperature, it was found that the dc joule-heated samples show relatively high GMR in comparison with furnace-annealed samples. Based on the phenomenological GMR model, we assumed that it is a consequence of smaller Co particles formed in dc joule-heated samples. © *1995 American Institute of Physics.*

I. INTRODUCTION

In recent years, the interest in giant magnetoresistance (GMR) and its physical origin was heightened by the observation of the GMR effect in ferromagnetic granular materials, in which magnetic single-domain clusters are embedded in a nonmagnetic metallic matrix.[1-6] It is now widely accepted that the GMR effect is associated with the reorientation of single-domain magnetic moments and has been interpreted on the basis of spin-dependent scattering. In magnetic granular systems, it has been shown that the spin-dependent scattering can occur in the magnetic clusters as well as at the interfaces between the magnetic and nonmagnetic phases and the interface scattering plays a dominant role due to the enhanced surface-to-volume ratio of the magnetic clusters.[7-9] More recently, melt-spinning has been shown to be a suitable method in preparing bulk GMR CoCu granular alloys.[10-12]

In this paper we report the GMR effect in magnetic granular Co$_{10}$Cu$_{90}$ alloys prepared by melt-spinning and subsequently annealed with direct-current (dc) joule heating. The dc joule heating was exploited to anneal the as-quenched CoCu samples by the effect of heat released by an electrical current flowing through a metallic material. Appropriately choosing electrical current and the treatment time, it is possible to perform annealing at higher temperature for shorter time with respect to conventional thermal treatments (furnace, DSC).[13,14] The related magnetic and structural properties are discussed.

II. EXPERIMENT

Metastable Co$_{10}$Cu$_{90}$ alloy was rapidly solidified by melt-spinning. 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 samples, clipped between the copper electrodes (electrode distance is 0.1 m), were submitted to an electrical current of constant intensity for 60 s. The electrical resistance R was continuously monitored by measuring the voltage drop across a standard resistor, in order to detect the structural change occurring in the sample. The as-quenched samples were also furnace annealed in vacuum of 2.0×10^{-5} Torr in comparison with dc joule heating. The samples were routinely subjected to x-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements. The magnetoresistance was measured using direct-current four-terminal geometry attached to a superconducting quantum interference device (SQUID) magnetometer in the magnetic field up to 50 kOe with the temperature change from 4.2 to 320 K.

III. RESULTS AND DISCUSSIONS

A. Co phase separation

The time behavior of the electrical resistance $\Delta R/R_0$ (R_0 being the room temperature resistance) for the Co$_{10}$Cu$_{90}$ samples is presented in Fig. 1. For the currents $I\leq3$ A, the $\Delta R/R_0$ reaches a steady value corresponding to the final sample temperature, which indicates that no transformation occurs in the samples. For higher currents, $I\geq4$ A, however, a significant reduction in R is observed after initial rise, and the resistance peaks become sharper

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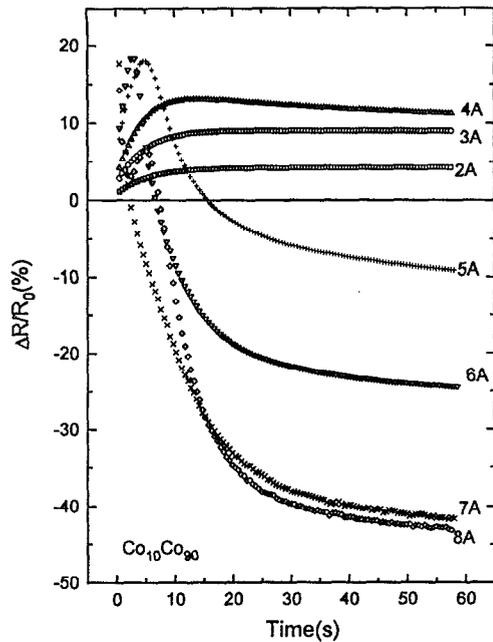
FIG. 1. Resistance vs time curves of $Co_{10}Cu_{90}$ samples submitted to different currents.

FIG. 2. DSC traces of as-quenched $Co_{10}Cu_{90}$ sample at the heating rates of 40, 80 and 160 °C/min.

with increasing currents. The resistance bumps observed during dc joule heating are associated with structural changes occurring within the samples, namely the precipitation and growth of the Co clusters. However, the curves are difficult to exactly analyze because the time behavior of the resistance during dc joule heating depends on several factors: change in the materials resistance during Co precipitation, change in the temperature coefficient of resistivity, and the extra heat released by Co precipitation, etc. The Co precipitation acts as a complete process, simultaneously producing a reduction in the resistivity of the samples. The final sample temperature results from the balance between the applied power and dissipation effects in the fully precipitated samples.

For the samples as-quenched and annealed with $I \leqslant 7$ A, the XRD experiments only show a distinct fcc pattern close to that of bulk Cu. As the annealing current is increased $I \geqslant 8$ A, a new fcc pattern corresponding to Co clusters is observed. The lattice constant for Co clusters in the sample annealed with $I = 8$ A is 0.3555 nm which is larger than the lattice constant of bulk Co, 0.3545 nm, due to the presence of Cu atoms in the Co clusters. The conventional XRD method is insensitive to the small Co precipitates formed at $I \leqslant 7$ A due to the high coherency between the Co and Cu phases. On the other hand, we found that DSC measurements are extremely sensitive to the Co precipitation process as shown in Fig. 2. The Co cluster precipitation starts at $T \approx 350$ °C, and finishes at $T \approx 700$ °C (beyond the maximum temperature of our DSC). Two exothermic peaks have been observed at temperatures shifting about 80 °C. The higher peak temperature is about 580 °C, where the XRD peaks for Co clusters begin to appear at d spacing. Thus, we assume that the Co particle precipitation should include two
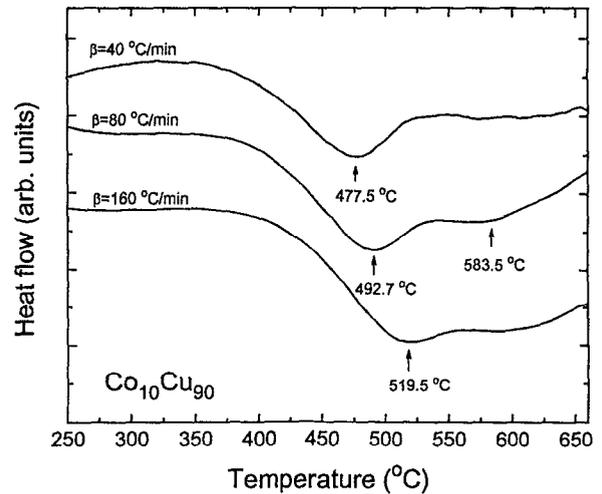
processes: (1) the nucleation of Co clusters, corresponding to the first peak; and (2) the growth of Co clusters (second peak). This process may result in the breakdown of the lattice coherency between two phases. We calculated the exothermic heat release of 2.00 kJ/mol which is lower than the heat of mixing of 4.20 kJ/mol for the $Co_{10}Cu_{90}$ alloy obtained by the thermodynamic data of the Co-Cu system.[15] The main difference of these two values is the consequence of the Co clusters formed during rapid solidification from the melt state.

B. The magnetic properties

Figure 3 shows the magnetization for the samples in both field-cooled (FC) and zero-field-cooled (ZFC) states in an appled field of 50 Oe. The ZFC peak occurs at 12.0 K for the as-quenched sample. Upon annealing with $I = 7$ A, the peak of the ZFC curve shifts to about 24.0 K. The higher ZFC peak temperatures reflect the Co particle growth during annealing. For $I = 8$, an abrupt change in the magnetic behavior is seen. In this case, the Co particles become large and exhibit reentrant magnetic or ferromagnetic behavior.[16] As observed in sputtered[1,5] and melt-spun[11] samples, a large thermal hysteresis was also observed for the annealed samples below a characteristic freezing temperature, where the 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.

The magnetization curves for the samples at 295 K are presented in Fig. 4. For the sample annealed at $I = 8$ A, the magnetization was found to be easily saturated. For the samples as-quenched or annealed at $I \leqslant 7$ A, the magnetization does not saturate even in the field up to 30 kOe. The saturation magnetization Ms primarily decreases with increasing annealing current and reaches the minimum value of 7.15 emu g^{-1} at $I = 4$ A, then increases to the maximum
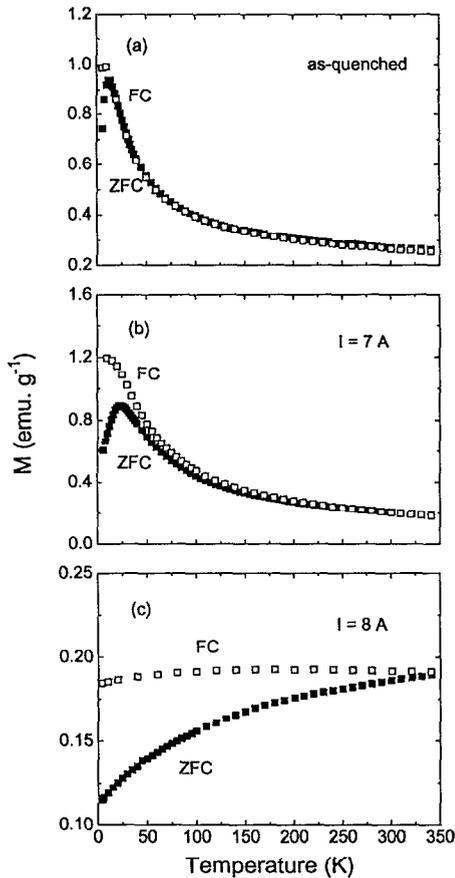
FIG. 3. Magnetization in 50 Oe for selected $Co_{10}Cu_{90}$ samples both in field-cooled (FC) and zero-field-cooled (ZFC) states: (a) As-quenched, (b) $I=7$ A, and (c) $I=8$ A.

value of 10.12 emu g^{-1} at $I=7$ A, and decreases again. The decrease of Ms for the sample annealed at low temperature has been found several times, but its physical origin is not clear at the moment. The decrease of Ms for the sample
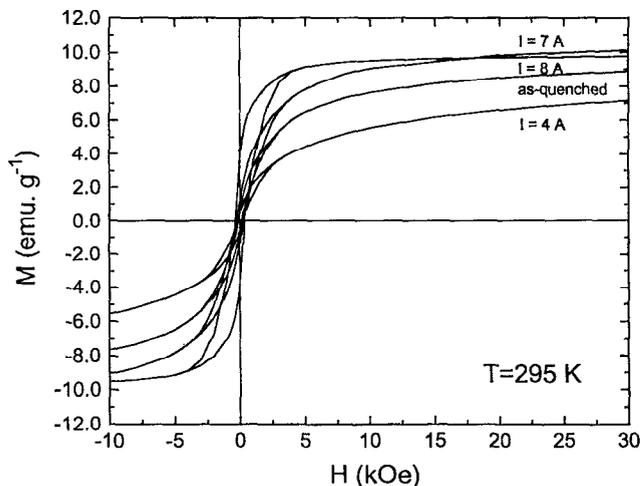

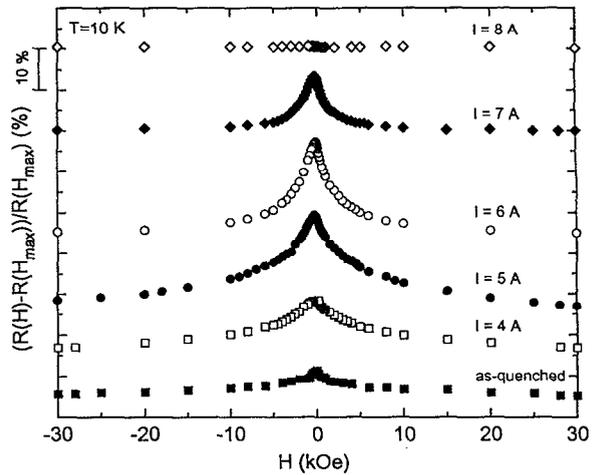FIG. 4. Room temperature $M(H)$ curves of selected $Co_{10}Cu_{90}$ samples.

FIG. 5. $\Delta R/R$ versus H for granular $Co_{10}Cu_{90}$ samples at 10 K.

annealed at high temperature may be related to the diffusion of Co atoms back to the Cu matrix,[17] it may be also related to the change of interface roughness.

C. The transport properties

Figure 5 shows the GMR values as a function of applied field at 10 K for the $Co_{10}Cu_{90}$ samples. The data are presented in the form of $\Delta R/R=[R(H)-R(H_{max})]/R(H_{max})$, where H_{max} is the maximum field. A characteristic of the samples as-quenched and annealed with low current is the lack of saturation in the GMR value at the maximum field of 30 kOe. In as-deposited $Co_{20}Cu_{80}$ film, there is no GMR (MR$\approx$0.5%) at 5 K.[2] In our experiments, however, a MR change of 6.5% 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 assumption that some Co particles have already been formed during rapid solidification. The optimum annealing current is about 5 A, where a MR change of 25.0% is achieved. Further increasing the annealing current, the GMR value drops due to the growth of Co particles.

The GMR in the maximum field of 30 kOe at 295 K is presented in Fig. 6 as a function of annealing currents and temperatures. The MR change in dc joule-heated samples was found to be higher than that observed in furnace annealed samples. The dependence of GMR on the annealing conditions is attributed to the microstructural change in the samples, mainly to the Co particle size and its distribution. Thus, determination of magnetic particle size and the size dependence of GMR is essential to understanding the origin of GMR in granular materials. Unfortunately, both XRD and TEM are insensitive to small Co clusters due to highly lattice coherency and small lattice mismatch ($<$2.0%). However, the magnetic Co particle size can be estimated by analyzing the experimental magnetic data. For small magnetic anisotropy, the cluster moment will exhibit a Boltzmann distribution of orientations with respect to the field H at thermal equilibrium. The magnetization M of a superparamagnetic system with uniform spherical particle size is then given by
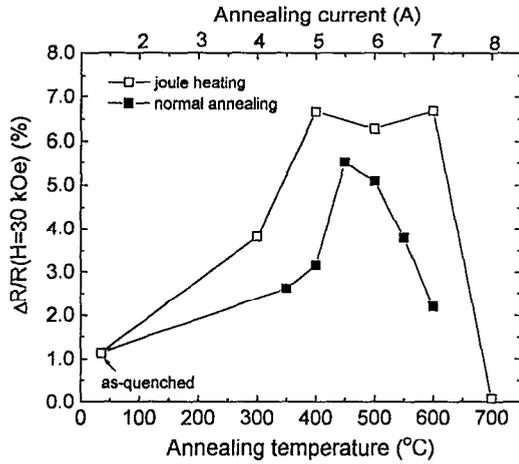
FIG. 6. The MR change for $H=30$ kOe in the $Co_{10}Cu_{90}$ alloys both annealed by dc joule heating and in a furnace.
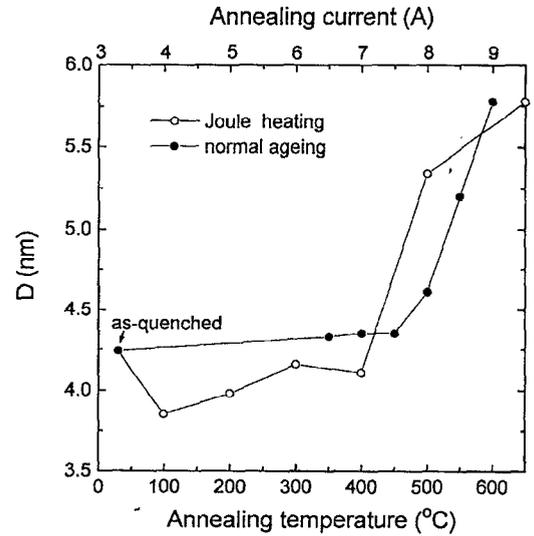

FIG. 7. The Co particle diameter as a function of annealing current.

the Langevin equation[18] $L(\alpha)=\coth(\alpha)-1/\alpha$. In the real system, it is necessary to consider a distribution in the particle sizes. Therefore, the magnetization of a magnetic granular system with magnetic particles of different sizes should be described by

$$M=pMs\int_0^\infty\left(\coth\frac{\mu H}{k_BT}-\frac{k_BT}{\mu H}\right)f(V)dV, \qquad (1)$$

where p is the volume fraction of Co particles, $\mu=MsV$ is the magnetic moment of a single-domain particle with volume V, H is the external field, and $f(V)$ is the particle size distribution. Assuming spherical particle of diameter D for simplicity, a log-normal size distribution

$$f(D)=\frac{1}{\sqrt{2\pi}\ln\sigma}\exp\left[-\frac{(\ln D-\ln\bar{D})^2}{2(\ln\sigma)^2}\right] \qquad (2)$$

is often used,[19] where $V=\pi D^3/6$. Using the 0 K and 295 K values of the saturation magnetization for pure fcc Co, 162.5 emu/g (1.435×10^3 emu/cm^3)[16] and 155.2 emu/g (1.371×10^3 emu/cm^3),[20] respectively. Fitting the experimental data $M(H)$ at room temperature to Eq. (1), the particle size distribution characterized by average diameter $\bar{D}$ and geometric standard deviation σ can be obtained. The average Co particle sizes are shown in Fig. 7. From Fig. 7, it was confirmed that the size of Co particles formed in dc joule-heated samples is smaller than that formed in furnace-annealed samples, which is likely the main reason why dc-joule heated samples exhibit higher GMR value.

Previous works on GMR suggested that the current is carried in two independent conduction channels corresponding to spin-up and spin-down electrons. The field dependence of the resistivity is attributed to the spin-dependent scattering within the magnetic particles and at the particle-matrix interfaces.[7,8] Figure 8 shows the Co particle size dependence of GMR measured at 10 K. The MR value decreases with increasing Co particle size. We have examined the MR dependence upon Co particle size by a phenomenological model:[7]

$$\Delta R/R=\frac{\left(\dfrac{2p_b}{\lambda_m}+\dfrac{6p_s}{r_m\lambda_s}\right)^2}{\left(\dfrac{1+p_b^2}{\lambda_m}+\dfrac{1-c}{c\lambda_{nm}}+\dfrac{3(1+p_s^2)}{r_m\lambda_s}\right)^2-\left(\dfrac{2p_b}{\lambda_m}+\dfrac{6p_s}{r_m\lambda_s}\right)^2}$$
$$\times[1-\alpha^2(H)], \qquad (3)$$

where c is the concentration of magnetic particles per unit volume, r_m is the average radius of the particles, p_b and p_s are the ratios of spin-dependent to spin-independent scattering potentials in the magnetic particles and at the particle-matrix interfaces, λ_s is a parameter representing the interfacial roughness, λ_m and λ_{nm} are the mean-free paths for magnetic particles and the nonmagnetic matrix, and $\alpha(H)=M(H)/Ms$. Using the data $\lambda_m=5$ nm and $\lambda_{nm}=25$ nm, and fitting the experimental data to Eq. (3), we
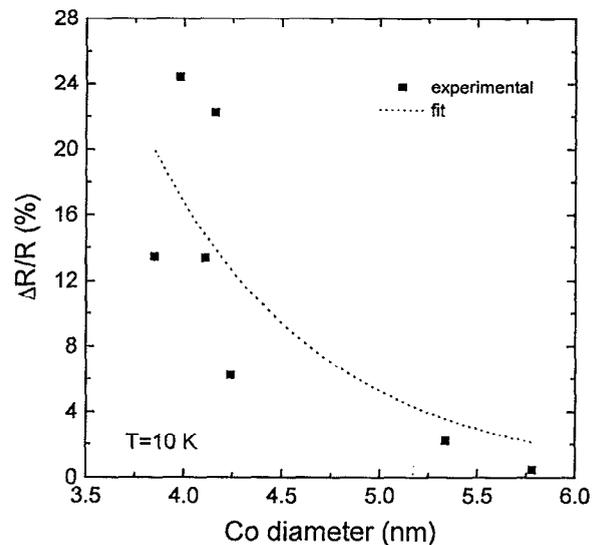

FIG. 8. The Co particle size dependence of the GMR effect for $Co_{10}Cu_{90}$ samples measured at $T=10$ K.

obtain $p_b = 0.16$, $p_s = 0.71$, and $\lambda_s = 4.5a_0$. The result of $p_s > p_b$ indicates that the interfacial spin-dependent scattering plays an important role in the GMR effect in granular systems, and which is consistent with previous works.[1,9] The dc joule heating is generally based on a higher heating rate (up to $10^4 - 10^6$ K/s under the current of 10 A), allowing the Co particles to be precipitated at a higher temperature for a short time. The Co cluster formation mechanism seems to be affected by dc joule heating in the way that the growth of the Co clusters, especially that formed during rapid solidification from the melt state,[21] was hindered during dc joule heating and a shorter time maintained at the highest temperature, which results in the finer Co cluster and higher GMR. According to the GMR model,[7,8] the main structural parameters influencing GMR are the particle size and the interfacial roughness. A clear relation between structure and the GMR effect in granular alloys is still absent at the moment. Thus, a detailed structural investigation is needed in order to clarify the origin of the GMR effect in granular systems.

IV. CONCLUSIONS

In conclusion, we have shown that the GMR effect can be achieved in melt-spun $Co_{10}Cu_{90}$ alloys annealed by dc joule heating. The GMR as large as 25.0% has been observed for the $Co_{10}Cu_{90}$ sample annealed at $I = 5$ A. The behavior of MR with changes in Co particle size fits the prediction of two-current assumption in which spin-dependent scattering is dominated by the particle-matrix interfaces. It was found that the dc joule-heated samples show a higher GMR effect than those furnace-annealed. We assume that it is attributed to the relatively small Co particle size formed in dc joule-heated samples.

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