Magnetic Properties and GMR Effect in Nonequilibrium Co-Cu Alloys Produced by Mechanical Alloying

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Co₂₀Cu₈₀ binary alloy is produced by mechanical alloying. The magnetoresistance (MR) and magnetic properties in temperature range from 5K to 300K, have been investigated for the as-milled and annealed alloys. The MR for the as-milled sample measured at the temperatures below 120K is not proportional to the square of magnetization M^2 . However, the MR for the annealed sample changes almost following M^2 even below this temperature. With decreasing temperature, the MR ratio for the as-milled sample slightly increases and becomes a constant value of about 3% below 180K, and for the annealed sample monotonously increases and shows about 14% at 5K.

Key words: mechanical alloying, Co-Cu alloy, magnetoresistance, zero-field-cooled magnetization, magnetization curve

1. Introduction

Research on the magnetism and electrical transport properties of nonequilibrium Co-Cu alloys has attracted attention in terms of the fundamental physics and applications. It is known that the magnetism of as-sputtered Co-Cu alloys in the low temperature range transits from reentrant spin glass state to spin glass orders with decreasing Co concentration¹⁾. Giant magnetoresistance (GMR) has been observed in the granular Co-Cu alloy which is phase-separated into two phases of ferromagnetic Co fine particles and nonmagnetic Cu matrix by annealing. GMR of about 7% at room temperature has been observed in the granular Co-Cu alloys, with Co concentration of about 20at%, prepared by the sputtering^{2,3)}. The value of the MR and the composition of the alloy showing the maximum MR were different for the various preparation methods^{4,5)}. The reason seems to be due to the difference in the precipitated grain size, distribution of the particles, and the microstructure depending on the preparation methods. The GMR effect is generally attributed to the spin-dependent scattering in the Co magnetic fine particles embedded in a nonmagnetic Cu matrix. It is thought that the MR is related with the magnetism; however, the details have not yet been clarified.

We have already reported that the Co₂₀Cu₈₀ alloy produced by mechanical alloying has a GMR of 6.7% at room temperature¹⁰⁾. In this work, we have examined the magnetic and electrical properties, at the temperatures from 5K to 300K, of the as-milled and annealed Co₂₀Cu₈₀ alloys produced by mechanical alloying, and have discussed the relationship between GMR and magnetic behaviors.

2. Experimental

Elemental Co and Cu powders were mechanically alloyed for 50 h. The Co concentration was fixed at

20at%. The compact of the mechanically alloyed powder was made using uniaxial-pressure-type press equipment, and was annealed at 723K for 1 h under 10^{-6} Torr. The magnetization in the temperature range from 5K to 300K was measured using a Quantum Design SQUID magnetometer. The ac susceptibilities were measured with an ac mutual inductance bridge operated at frequency of 80 Hz with an ac-field of 10 Oe. Magnetoresistance (MR) was measured under magnetic fields up to 17 kOe in the temperature range from 5K to 300K using dc four probe method with the current perpendicular to the direction of the applied field. MR ratio was calculated as $|\Delta R/R_0| = (R_H - R_0)/R_0$, where R_H is the resistance due to the applied field and R_0 is the maximum resistance near zero field.

3. Results and discussion

Fig. 1 shows the temperature dependence of zero-field-cooled magnetization per unit applied magnetic field (ZFCM/H) and ac linear magnetic susceptibility (χ_0) for the Co₂₀Cu₈₀ alloys in the as-milled state and after annealing at 723K. The ZFCM of the as-milled sample measured at 100 Oe exhibits a peak, and shows a plateau below the peak temperature. The ZFCM curve shows reentrant spin-glass-like behavior. At a lower field, the plateau becomes clearer, and the temperature showing the peak of the ZFCM shifts toward higher temperature side. The temperature dependence of the ZFCM at various applied magnetic fields are similar to the results reported for the alloys prepared by sputtering¹⁾. However, the Co concentration (20at%) at which the reentrant behavior is observed for our as-milled sample is lower than that

Fig. 1 Temperature dependence of the zero-field-cooled magnetization per unit applied magnetic field (ZFCM/H) and the ac linear magnetic susceptibility (χ_0) for Co₂₀Cu₈₀ alloys in the as-milled state and after annealing at 723K for 1 h.

Fig. 2 Magnetization curves measured at the temperatures from 5K to 300K, for $\text{Co}_{20}\text{Cu}_{80}$ alloys in the as-milled state and after annealing at 723K.

(~25at%) of the as-sputtered alloy. The reason for this difference in the composition seems to be due to the difference of mixing or diffusion states of Co and Cu depending on the preparation methods. The ZFCM of the sample annealed at 723K, exhibits a broad peak and increases at higher temperature side. A similar temperature dependence of ZFCM was observed when the applied magnetic field is reduced from 100 to 10 Oe. The reason for this broad peak seems to be that the Co particles precipitated in the Cu matrix have a wide distribution of particle size with various blocking temperatures. Using the magnetic anisotropy constant of the fcc Co¹¹⁾, we estimate the average size of the particles from the blocking temperature to be about 70 Å in diameter for the annealed sample. However, this estimated value depends on stress, shape and surface effect of the magnetic particles¹²⁾. The above results are similar to the temperature dependence of ac linear magnetic susceptibility for the as-milled and annealed samples, as shown in Fig. 1.

Fig. 2 shows the magnetization curves measured at various temperatures in the range from 5K to 300K, for the as-milled and annealed samples. The magnetization curves of the as-milled sample show hysteresis at the temperatures below 120K, but the hysteresis was not observed at the temperatures above 180K. On annealing the sample the magnetization increases, and the hysteresis of the magnetization curve decreases with increasing measurement temperature and becomes negligibly small at 300K.

It is well known that the $M-H/T$ curves for temperatures above the temperature of the peak value in the ZFCM curve should coincide with each other, in

Fig. 3 Magnetization (M) for as-milled and annealed samples, as a function of H/T .

case of superparamagnetism¹³⁾. Fig. 3 shows the magnetization (M) for the as-milled and annealed samples as a function of H/T . The $M-H/T$ curves for the as-milled samples do not coincide, which indicates that the sample is not paramagnetic, rather superparamagnetic having ferromagnetic fine clusters. The magnetism of the clusters perhaps depends on temperature, and therefore $M-H/T$ becomes different curves¹²⁾. The $M-H/T$ curves of the annealed sample measured at higher temperature (~200K) almost coincide with each other. From this coincidence of $M-H/T$ curves and the existence of a peak in ZFCM curve (Fig. 1) it can be concluded that the magnetism of the annealed sample has superparamagnetic behavior at higher temperature. If it is considered that the blocking temperature corresponds to the volume of the magnetic particle¹⁴⁾, then the large magnetic particles having blocking temperature above room

Fig. 4 Field dependence of the $\Delta R/R_0$ for as-milled and annealed samples.

Fig. 5 Temperature dependence of the MR ratio for as-milled and annealed samples prepared by mechanical alloying (solid lines), and for as-sputtered and annealed samples prepared by sputtering (broken lines, from Ref. 2).

temperature will show ferromagnetic property at room temperature. This corresponds to the slight hysteresis which is observed in the magnetization curve measured at 300K, as shown in Fig. 2. Since the hysteresis is very small, therefore it could be considered that the volume fraction of the ferromagnetic particles is very small.

Fig. 4 shows the field dependence of $\Delta R/R_0$ for the as-milled and annealed samples. The magnetic field dependence of $\Delta R/R_0$ measured at the temperatures from 5K to 180K for the as-milled sample almost coincide in a single line. However, the $\Delta R/R_0$ for the annealed sample largely depends on the measurement temperature even in this temperature range.

Using the data of Fig. 4, the temperature dependence of the MR ratio (at 17 kOe) is shown in Fig. 5. with additional data for the as-milled sample with 15at%Co. The MR ratio of the as-milled sample slightly increases with decreasing temperature, and becomes constant (~3%). The MR ratio of the annealed sample increases with decreasing temperature, and shows about 14% at 5K. Compared with the results of the sputtered samples²⁾, our annealed sample exhibits a similar tendency, however, the as-milled sample does not. The reason for the difference between the temperature dependence of the MR ratio for our mechanically alloyed sample and that of the as-sputtered sample is due to the difference in solid solution state and the composition distribution. The MR ratio for the as-milled sample with 15at%Co increases with decreasing temperature as shown in the Fig.5.

In Fig. 6, we show the relationship between the $\Delta R/R_0$ and the M which are measured at various applied magnetic fields, by using the data of Figs. 2 and 4. The $\Delta R/R_0$ of the as-milled sample measured at the temperatures from 180K to 300K, changes following M^2 . The $\Delta R/R_0$ at the temperatures below 120K is not proportional to M^2 . That is, the $\Delta R/R_0$ shows a constant small value though the magnetization increases i.e. this change in the magnetization in small magnetic field corresponds to the hysteresis region as shown in Fig. 2. This means that the $\Delta R/R_0$ has not been affected by the ferromagnetic component. In the annealed sample, the $\Delta R/R_0$ measured at the temperatures from 50K to 300K is almost proportional to M^2 . However, the

Fig. 6 Relationship between the $\Delta R/R_0$ and the magnetization (M) for as-milled and annealed samples.

proportionality constant depends on the measurement temperature. The reason can be explained by the fact that the R_0 decreases with decreasing temperature¹⁵⁾.

The magnetization of the ferromagnetic component i.e., the hysteresis part observed at low temperature (Fig. 2) hardly contribute to the MR ratio of the as-milled sample, but contribute to the MR ratio of the annealed sample. The ferromagnetic component of the magnetic particles or clusters for the as-milled and annealed samples shows different magnetic and electric properties depending on their shape, size and composition, and contributes to the magnetoresistance effect in different process.

References

- 1) J. R. Childress and C. L. Chien: *Phys. Rev. B*, **43**, 8089 (1991).
- 2) A. E. 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).
- 3) J. Q. Xiao, J. S. Jiang, and C. L. Chien: *Phys. Rev. Lett.*, **68**, 3749 (1992).
- 4) J. Wecker, R. von Helmolt, L. Schultz, and K. Samwer: *IEEE Trans. Magn.*, **29**, 3087 (1993).
- 5) N. Kataoka, H. Endo, K. Fukamichi, and Y. Shimada: *Jpn. J. Appl. Phys.*, **32**, 1969 (1993).
- 6) R. J. Gambino, T. R. McGuire, J. M. Harper, and C. Cabral, Jr.: *J. Appl. Phys.*, **75**, 6909 (1994).
- 7) Y. Ueda and M. Ito: *Jpn. J. Appl. Phys.*, **33**, L1403 (1994).
- 8) H. Zaman, A. Yamada, H. Fukuda, and Y. Ueda: *J. Electrochem. Soc.*, **145**, 565 (1998).
- 9) T. Sugawara, K. Takanashi, and H. Fujimori: *J. Magn. Soc. Jpn.*, **21**, 469 (1997).
- 10) Y. Ueda, S. Ikeda, and S. Chikazawa: *Jpn. J. Appl. Phys.*, **35**, 3414 (1996).
- 11) R. H. Yu, X. X. Zhang, and J. Tejada: *J. Appl. Phys.*, **78**, 392 (1995).
- 12) B. J. Hickey, M. A. Howson, D. Greig, and N. Wiser: *Phys. Rev. B*, **53**, 32 (1996).
- 13) G. T. Rado and H. Suhl: *Magnetism*, Vol. 3, p.272 (Academic Press, New York, 1963).
- 14) T. Bitoh, K. Ohba, M. Takamatsu, T. Shirane, and S. Chikazawa: *J. Magn. Magn. Mater.*, **154**, 59 (1996).
- 15) Y. Ueda and S. Ikeda: in preparation.