Magnetic properties of metallic Co- and Fe-based granular alloys

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We have studied the magnetic properties of Co-Ag and Fe-Ag granular alloys made using vapor-quenching techniques and thermal annealing. Magnetic coercivity (H_c) and remanence can be controlled over a large range by varying annealing temperature and particle volume fraction. A large H_c on the order of 2 kG has been obtained in the Co-Ag system. We have investigated magnetic anisotropy, the effect of particle size, and coalescence in these nanostructured materials.

Magnetic granular solids have received considerable attention in the past few years.[1–10] In these composite materials, ultrafine magnetic particles of a few nanometers in size are embedded in a metallic or insulating matrix by certain synthesis processes. Because of their microstructure and the tunability in materials and geometrical parameters, these materials possess different and sometimes enhanced properties when compared with their bulk counterparts. In particular, a giant magnetic coercivity (H_c) has been achieved in Fe-SiO_2 granular films,[1] with H_c enhanced by as much as three orders of magnitude over the bulk value. The large H_c and magnetization of the material make it suitable for application in magnetic recording. It has also been discovered that metallic granular alloys, such as Co-Cu, Co-Ag, and Fe-Ag, exhibit giant magnetoresistance effects (GMR),[6–10] with a magnitude rivaling the best multilayers with GMR. These developments in granular solids call for more systematic studies of their magnetic properties. The understanding of the novel GMR effect also requires the exploration of the underlying magnetic state which strongly correlates with the behavior of GMR. In this work, we present a study on two transition metal granular solids, Co-Ag and Fe-Ag, both of which have been shown to have GMR effect.[8–10] The main focus here is how the thermal treatment and volume fraction of the magnetic particles affect the magnetic properties.

We have fabricated Co-Ag and Fe-Ag granular films by taking advantage of the immiscibility between Co (or Fe) and Ag in alloy formation. High vacuum sputtering from a cold-pressed composite target yields a phase-separated film with magnetic particles precipitating from the Ag matrix. The particle size of an as-sputtered sample is very small, on the order of 1–2 nm. We have also fabricated samples using codeposition technique and obtained similar physical properties. Thermal annealing is an effective means to enlarge the particle size. We have prepared a series of samples with different thermal annealing as well as varying volume fraction. Phase separation has been confirmed by using a combination of analysis, i.e., transmission electron microscopy (TEM), x-ray diffraction, and magnetic susceptibility measurement. Detailed results will be presented elsewhere.[11] Analysis of phase separation for the Co-Ag system can also be found in Ref. 12.

We used a superconducting quantum interference device (SQUID) magnetometer to measure the magnetic hysteresis curve of our samples. Since we are interested in the ground state properties, most of our measurements were carried out at low temperatures. The saturated magnetization of the magnetic component (Fe or Co) is approximately equal to that of the bulk. In addition to magnetic measurements, we have also performed magnetoresistance and Hall effect measurements. Both Fe-Ag and Co-Ag show GMR effect and extraordinary Hall effect.[8–10] The Hall resistivity can be described by $\rho_{xy}=\rho_{xy}^0+R_sM$. In this relation, ρ_{xy}^0 is due to the ordinary Hall effect and is linear in magnetic field. The second term, due to the extraordinary Hall effect,[13] results from the left–right asymmetry in electron scattering in magnetic systems. Because of its linear relationship with M, the field dependence of ρ_{xy} after removing ρ_{xy}^0 shows a one-to-one correspondence with the magnetic hysteresis curve. Therefore, when the sample plane is perpendicular to the external magnetic field, we can consistently obtain remanent magnetization and coercivity from either Hall effect or magnetization measurements. It is noted that it is more efficient and economical to measure the Hall effect than the magnetization using a SQUID magnetometer.

Figure 1 shows the magnetization curves at $T=5$ K for two representative as-prepared samples, $Co_{20}Ag_{80}$ and $Fe_{20}Ag_{80}$, with H perpendicular and parallel to the sample plane (both samples are specified by volume fractions of their components). The initial susceptibility measurement indicates that the superparamagnetic transition temperature is about 20–30 K. Therefore, at 5 K, the magnetic moment vectors of the particles are fixed in random directions. As shown in Fig. 1, the $Co_{20}Ag_{80}$ sample has a much larger H_c than the $Fe_{20}Ag_{80}$ sample. Most interestingly, the easy axis tends to be out of plane for Co-Ag, whereas it is in plane for Fe-Ag.

The anisotropy in Co-Ag is most likely caused by the crystalline and shape anisotropies of the Co particles. The maximum H_c which could result from crystalline or strain anisotropy is about 2900 (fcc) or 600 G respectively.[14] The large perpendicular H_c value of about 2 kG seen in Fig. 1 can be accounted for by magnetocrystalline anisotropy. The perpendicular H_c in Co-Ag is larger than the parallel H_c. To account for the observed perpendicular H_c in Co-Ag, it is reasonable to conjecture that the Co particles are slightly enlongated along the growth direction. Another possible source of anisotropy is from the interface between the magnetic particles and the surrounding Ag matrix. Because of the

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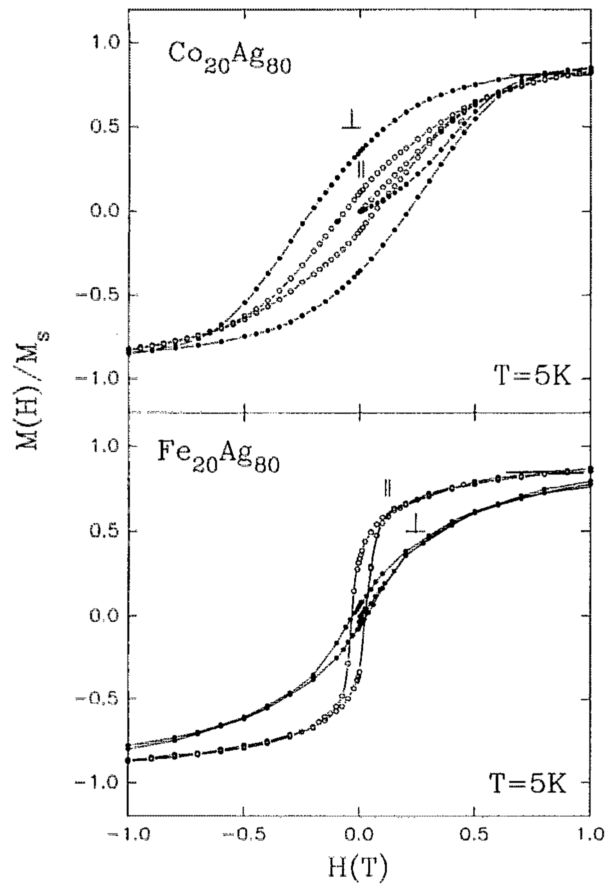

FIG. 1. Magnetic hysteresis curves in perpendicular and parallel field configurations for $Co_{20}Ag_{80}$ (upper panel) and $Fe_{20}Ag_{80}$ (lower panel) at T=5 K.

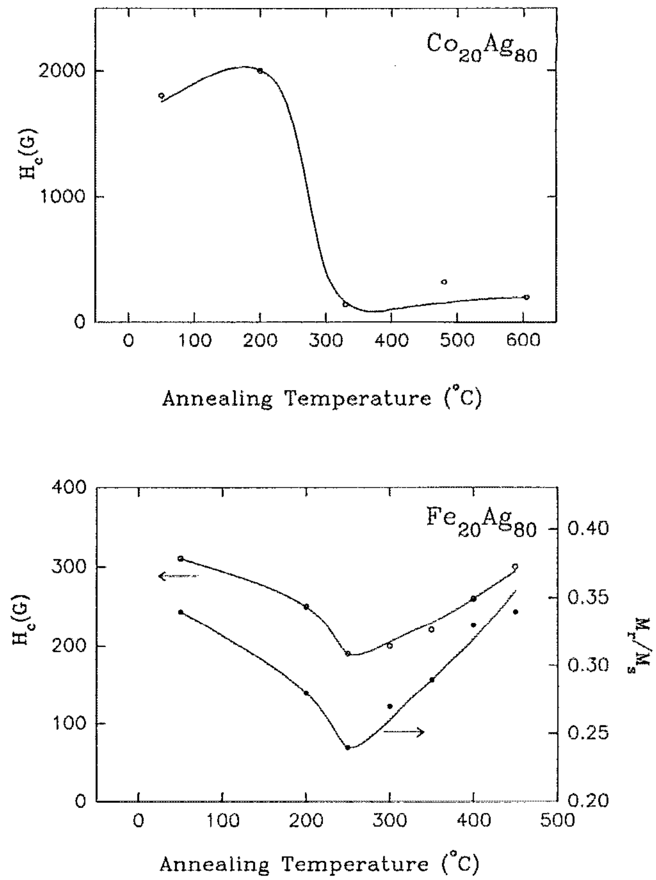

FIG. 2. Coercivity H_c vs annealing temperature T_A for $Co_{20}Ag_{80}$ (upper panel) and $Fe_{20}Ag_{80}$ (lower panel). Also shown in the lower panel is the remanence M_r/M_s for $Fe_{20}Ag_{80}$. T=5 K.

small size of the particles, interfacial effect could play an important role. Nevertheless, without the proposed growth texture, it is difficult to imagine how the interface anisotropy could cause the observed perpendicular anisotropy under the influence of the large demagnetization field of the thin film.

The H_c for the Fe-Ag system is of the magnitude of 300 G. While it is considerably larger than that of a polycrystalline Fe film (a few tens of G), it is much below the limit of crystalline (540 G) and strain (600 G) anisotropy for single-domain particles.[14] The shape anisotropy in Fe can provide a maximum H_c of 10.7 kG,[14] although experimentally such a large H_c in single-domain Fe particles has never been discovered. In Fe-SiO_2 granular films, a maximum H_c value of about 3 kG has been observed,[1] where the Fe particle size is about 50 Å. We have obtained the particle sizes in our $Fe_{20}Ag_{80}$ samples using both TEM and analysis of superparamagnetic behavior.[11] The $Fe_{20}Ag_{80}$ sample used for Fig. 1 has an average particle size of 29 Å. Thermal annealing at 300 °C enlarges the particle size to 51 Å, but the H_c was found to decrease to about 200 G. The comparison between Fe-Ag and Fe-SiO_2 granular systems shows convincingly that particle-matrix interface could be one of the important factors in the magnetic anisotropy of Fe-based systems.

Among the magnetic parameters of a ferromagnetic solid, the ground state magnetization is basically an intrinsic parameter, whereas H_c and remanence M_r/M_s are primarily extrinsic parameters. They are sensitive to disorder, stress, and particle morphology. Thermal treatment is an effective means to induce phase separation, to enlarge particle size, and to reduce crystalline disorder and stress in granular materials. In Fig. 2, we present the results of annealing on H_c for $Co_{20}Ag_{80}$ and $Fe_{20}Ag_{80}$. Also included in Fig. 2 is an annealing temperature (T_A) dependence of M_r/M_s for $Fe_{20}Ag_{80}$. Thermal annealing was done in high vacuum (1×10^{-7} Torr) at a chosen T_A for 15 min, followed by natural cooling. From the TEM micrograph, it was found that the Co particle size increases from about 20 to 130 Å as T_A reaches 605 °C. X-ray diffraction revealed that the Co particles have fcc structure and are [111] textured.[8]

As shown in Fig. 2, H_c for $Co_{20}Ag_{80}$ drops by a large amount once T_A exceeds 250 °C. This variation of H_c has been verified more than once. Such a drop in H_c is desirable because it tends to reduce the saturation field and hysteresis in GMR effect, which was indeed observed.[8] There are a few possible causes for this drop. First of all, it is not due to the enlarged particle size which may induce multidomain formation and reduce H_c. Within our T_A range, the Co particle size is always below the critical single-domain particle size.[14] Most likely, as the particle size grows, the original growth texture diminishes, which reduces the particle shape anisotropy. Another possible cause is that annealing makes phase separation more complete and tends to reduce crystalline disorder and stress. Both effects will reduce pinning force for magnetization, and, therefore, lower H_c.

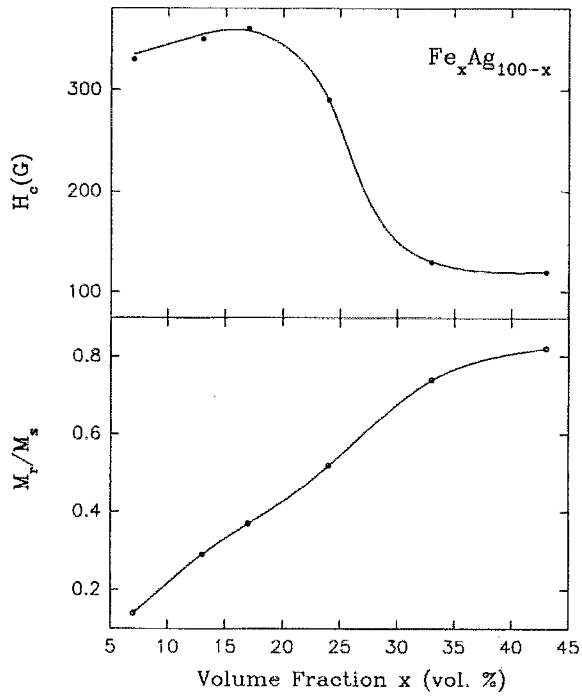

FIG. 3. Coercivity H_c (upper panel) and remanence M_r/M_s (lower panel) for Fe_xAg_{100-x} alloys as functions of volume fraction x. T=5 K.

The variation of H_c with T_A for $Fe_{20}Ag_{80}$ resembles the behavior in $Co_{20}Ag_{80}$, in that we see a similar drop in H_c near 250 °C. However, beyond 250 °C, H_c increases as Fe particles become larger. The remanence has a similar dip near 250 °C. Particle size analysis shows that the Fe particle size steadily increases from 21 Å in the as-sputtered sample to 71 Å at the maximum T_A of 400 °C. All are considered as single-domain particles.[14]

The above results reveal that thermal annealing has the universal effect of increasing particle size, however, its role on H_c is not straightforward, but is material dependent in metallic granular solids. At present, the cause for these diverse observations is not clear. However, it is important to remember that there are many sources at play for H_c, almost all are affected to varying degrees by thermal annealing.

Earlier studies have shown that thermal annealing substantially *enhances* H_c of various Fe-[2,4] and Co-based[3,4] granular solids. This is in sharp contrast with the behaviors of our Fe-Ag and Co-Ag systems, where moderate annealing depresses H_c. The difference is due to the fact that the earlier studies were performed at room temperature, whereas ours are at low temperature. At T=300 K, thermal relaxation reduces H_c severely for moderately annealed samples where the magnetic particles are small in size. In fact, any superparamagnetic sample has zero hysteresis. For samples annealed at high temperatures, and therefore, having large particle size, thermal agitation is less important, and H_c appears higher. In order to eliminate the effect of thermal relaxation, measurements need to be done at low temperatures.

Next we turn our attention to the effect of particle volume fraction (x) on magnetic properties. Here, x was determined from the composition and the bulk density of each component. Figure 3 shows H_c and M_r/M_s as functions of x for the Fe_xAg_{100-x} as-sputtered system. In the low x region (x<0.2), H_c remains relatively constant. Starting at $x \sim 0.2$, H_c gradually decreases, approaching the bulk value of polycrystalline Fe. M_r/M_s, on the other hand, increases smoothly with x in the whole x range studied. The evolution of H_c and M_r/M_s with x is the result of the transition from an assembly of almost independent particles to a network of connected particles. As x increases, there is an increasing coalescence of magnetic particles. In fact, above the percolation threshold x_c, cluster network of infinite extension is formed. Beyond this limit, the granular solid becomes increasingly bulk-like, and bulk polycrystalline Fe film is characterized by low H_c and large remanence.

For a random three-dimensional system, the percolation threshold x_c is near 0.2. In our granular material, H_c starts to decrease at almost the same x. We have also measured the GMR effect ($\Delta\rho/\rho$) as a function x.[10] $\Delta\rho/\rho$ exhibits a peak at x=0.2, coinciding with the peak of H_c. This is because both GMR and H_c are sensitive to multidomain or cluster formation in a granular solid.

In summary, ground state magnetic properties have been measured for Co-Ag and Fe-Ag granular alloys which exhibit GMR. The Co-Ag films have a perpendicular magnetic anisotropy, whereas the easy axis of the magnetization of the Fe-Ag films is in-plane. The large H_c and perpendicular anisotropy in Co-Ag are attributed to the crystalline anisotropy and the enlongation of Co particles in the growth direction. Thermal annealing affects H_c profoundly in both systems. This cannot be explained by the monotonical increase of magnetic particle size. Other mechanisms such as phase separation, effect of disorder, and evolution of particle shape need to be considered. It is also found that coalescence of particles reduces H_c.

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