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Magnetic and magnetoresistive properties of mechanically alloyed $Fe_{25}Cu_{75}$

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Abstract. $Fe_{25}Cu_{75}$ samples were prepared by mechanical alloying followed by annealing. Mössbauer and magnetic measurements indicate superparamagnetic behaviour of the as-milled sample, probably due to the existance of Fe-rich regions in the FCC Cu matrix. Annealing causes the formation of α-Fe, which precipitates from Fe atoms dissolved in the FCC Cu phase. Magnetoresistance measurements for the as-milled sample show a 5.6–7.3% drop in resistance at 300 K and 50 K respectively, in applied fields of 12 T.

1. Introduction

Giant magnetoresistance (GMR), the large drop in resistance of a sample in an applied magnetic field, was shown to exist in Fe/Cr thin-film magnetic superlattices by Baibich *et al* [1], where, in their original work, the ferromagnetic Fe layers were separated by non-magnetic Cr 'spacer' layers. The GMR in this system was found to be approximately 50%, although GMR values of 65% at room temperature and 115% at 4.2 K were subsequently observed in Co/Cu multilayers [2]. Other multilayers were also found to exhibit significant GMR at room temperature, including Ni–Fe/Cu, Co/Ru, Co/Cr, Fe/Cr and Ni–Fe/Co/Cu [3–5].

The GMR in these systems is reputedly due to the spin-dependent electron scattering at the surface of adjacent layers [6], this being fundamentally different to 'classical' magnetoresistance (the Hall effect), which is a bulk effect [7].

Recent work on non-multilayered, magnetically inhomogeneous systems has shown that there is GMR present in granular systems consisting of immiscible binary alloys, wherein ferromagnetic grains are embedded in a non-magnetic matrix [8, 9]. The GMR in such systems is dependent upon the size of the magnetic particles, local magnetization of ferromagnetic entities and the angle that the local magnetization vector of ferromagnetic particles makes with the direction of the applied field [9].

Although much of this work has focused upon non-multilayered sputtered films of Co/Cu and Fe/Cu due to the relative immiscibility of these binary systems and the ease with which it is possible to obtain nanoscale Fe or Co particles in the Cu matrix [8, 9], work on granular systems prepared by melt spinning and mechanical alloying has shown that these systems also display GMR. For instance, GMR of up to 36% at 30 K in an applied field of 7.5 T was observed in melt-spun Co–Cu [10] and a 6.7% effect at 5 K and 7 T was observed in mechanically alloyed metastable Co-Au [11].

In general, mechanical alloying of the immiscible Fe–Cu system results in the formation of one of two phases: for an initial composition of 50 at.% Fe or less in Cu, mechanical

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alloying results in a supersaturated FCC Cu phase containing dissolved Fe atoms. For 70 at.% Fe or more, the result is a supersaturated BCC Fe phase containing dissolved copper atoms. These supersaturated phases are known to have a nanocrystalline structure [12, 13].

In this paper, we present an investigation of magnetic and magnetoresistive properties of 25 at.% Fe in Cu binary alloy, and show that the magnetoresistance of the sample is dependent upon temperature. Magnetic properties of the sample are also discussed in relation to the structure and annealing temperature (T_a) of the sample.

2. Sample preparation

Mechanical alloying was used for production of the samples. 10 g of elemental Fe and Cu with a composition of $Fe_{25}Cu_{75}$ were loaded together with 10 steel balls of diameter 12 mm, with a charge ratio (mass of balls:mass of sample) of 8:1. Mechanical alloying was carried out for 20 h using a Spex 8000 mixer/mill. Powders were heat treated under a vacuum of 1×10^{-6} Torr for 1 h at various temperatures between 100 and 600 °C.

Powders were studied using a Perkin Elmer DSC-4 differential scanning calorimeter. The structure was analysed using x-ray diffraction (Siemens D5000 diffractometer with Cu Kα radiation) and Fe^{57} Mössbauer techniques (Canberra Packard).

Magnetic and magnetoresistance measurements were performed on cold-pressed pellets (of cylindrical shape with diameter about 5 mm, and height from 0.5 to 1 mm) with densities of approximately 7.4 g cm^{-3} (theoretical density of Cu, 8.92 g cm^{-3}). Annealed pellets to be used for magnetoresistance measurements were heat treated at 200 °C for $\frac{1}{2}$ h under a vacuum of 1×10^{-6} Torr. Magnetic measurements were performed at various temperatures ranging from 50 K to 350 K using a vibrating sample magnetometer (VSM 3001 Oxford Instruments) with a maximum applied field of 12 T. Resistance data were obtained using the four-terminal method, with field applied perpendicular to the current direction.

3. Results and discussion

3.1. Structure

3.1.1. X-ray diffraction. X-ray diffraction studies showed only an FCC-phase for the as-milled powder (figure 1), with an estimated lattice constant of 3.631 Å. Transmission electron microscopy studies showed a nanocrystalline structure with grain sizes ranging between 5 and 10 nm [14]. These results are consistent with a supersaturated FCC Cu phase containing about 25% Fe, as prepared by mechanical alloying [15, 16].

The annealed powders were found to contain a mixture of α-Fe (BCC) and supersaturated FCC Cu containing dissolved Fe (figure 1). The amount of α-Fe increased with annealing temperature, and the lattice constant of the FCC Cu phase decreased, indicating that the amount of Fe dissolved in the FCC Cu phase was decreasing [15, 16]. For the sample annealed at 600 °C for 1 h, intensity ratios of the peak (111) reflection for the α-Fe phase and the (200) reflection for the FCC Cu phase (figure 1) agreed well with the 25% : 75% ratio of Fe to Cu present in the powder, with the lattice constant of the FCC Cu phase being identical to that for pure Cu.

It is noteworthy that the γ-Fe phase (FCC), which was found in the Mössbauer spectra, was not observed in any of the x-ray diffraction patterns, probably because of its low fraction, which is not detectable by x-ray diffraction. The largest fraction of γ-Fe was 2–3 wt% of the sample, found after annealing at 400 °C, which corresponds to 11% of Fe atoms as calculated from analysis of the Mössbauer spectrum.

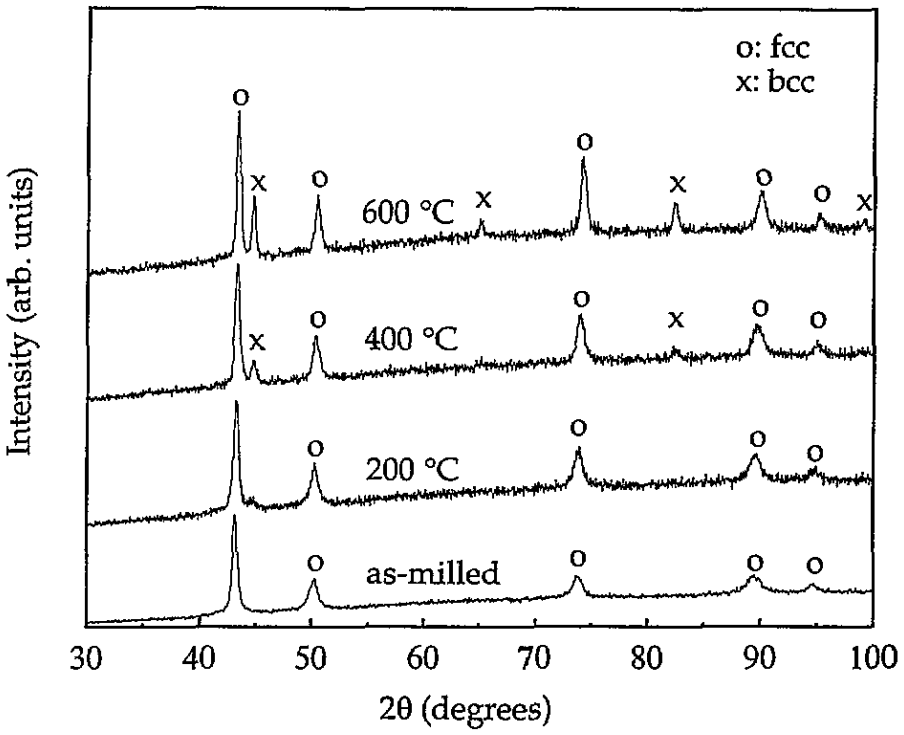

Figure 1. X-ray diffraction plots of the as-milled and annealed powders.

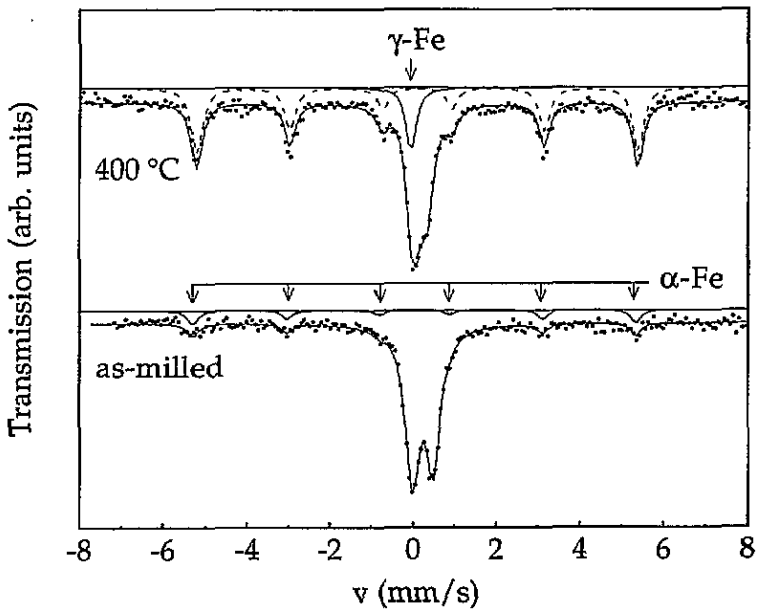

Figure 2. Mössbauer plots of the as-milled and 400 °C annealed powder.

3.1.2. Mössbauer spectroscopy. For the as-milled powder, about 7% of the total number of Fe atoms (about 2 wt% of the sample) were found in the α-Fe phase, and about 4% of Fe atoms (about 1 wt% of the sample) in the γ-Fe phase (as characterized by an isomer shift of -0.09 mm s^{-1} [13, 17]). The remaining Fe atoms dissolved in the FCC Cu phase (about 89% of the total) were identified by a doublet with an isomer shift of 0.22 mm s^{-1} and a quadrupole splitting of 0.49 mm s^{-1}. These results indicate that Fe atoms dissolved in the FCC Cu phase exhibit either paramagnetic or superparamagnetic behaviour at room temperature.

A Mössbauer spectrum of the as-milled powder taken at 77 K showed magnetic splitting of Fe atoms dissolved in the FCC Cu phase with a broadened distribution of hyperfine fields, the average hyperfine field being about 200 kOe, in good agreement with that measured for materials of similar composition at 4.2 K [18].

Mössbauer spectra of the annealed powders showed that there was no significant change (compared to the as-milled powder) after annealing at temperatures of 200 °C or less.

Annealing at 300–400 °C resulted in an increase of the α-Fe phase and an increase of the γ-Fe phase. About 11% of the Fe atoms were estimated to be in the γ-Fe phase after annealing at 400 °C. Higher annealing temperatures ($T_a \geqslant 450$ °C) led to a rapid increase of α-Fe, as seen in the x-ray diffraction plots (figure 1).

In the Mössbauer spectrum for the 600 °C annealed powder, more than 95% of the Fe atoms were found in the α-Fe phase. However, traces of a non-magnetic singlet and doublet in the Mössbauer spectrum indicate that the formation of α-Fe was not complete even after annealing for 1 h.

All of the Mössbauer parameters (hyperfine field, chemical shift and quadrupole splitting) for the three phases discussed above, were the same for both annealed and as-milled samples.

3.1.3. Differential scanning calorimetry. The formation of α-Fe and γ-Fe was monitored by differential scanning calorimetry measurements. A small, broad peak around 300 °C (figure 3, region A) corresponded to the formation of γ-Fe. The rapid increase of the α-Fe phase after heating at $T_a \geqslant 450$ °C was characterized by the large and broad peak at 550–580 °C (figure 3, region B). The formation of γ-Fe at lower temperatures and α-Fe at higher temperatures has been previously reported in mechanically alloyed Cu–Fe [13, 15, 19].

3.2. Magnetic measurements

Hysteresis loops of as-milled and annealed powders are shown in figure 4. It was not possible to fit the magnetization curve for the as-milled powder with a curve consisting of a ferromagnetic component (α-Fe) and a paramagnetic component (γ-Fe singlet, and doublet for Fe dissolved in the FCC Cu phase, as found in the Mössbauer study). The small amount of α-Fe (about 2 wt%) should give a contribution of about 5 A m^2 kg^{-1} to the total magnetization, which should be saturated in low fields because of the soft magnetic properties of α-Fe. This value of 5 A m^2 kg^{-1} is far below the measured magnetization of 19 A m^2 kg^{-1} at 2 T (figure 4) and 32 A m^2 kg^{-1} at 12 T. Furthermore, the magnetization could not be saturated with a maximum applied field of 12 T. The magnetic and Mössbauer studies of the as-milled powder indicate that the supersaturated FCC Cu phase (with a composition of about 25% Fe and 75% Cu) is superparamagnetic at room temperature.

The as-milled powder was measured at low temperatures [14]. The magnetic curves taken at 40 and 100 K exhibited ferromagnetic behaviour, such that the magnetization could be easily saturated with a relatively low field of 0.5–1 T. The magnetization measured at

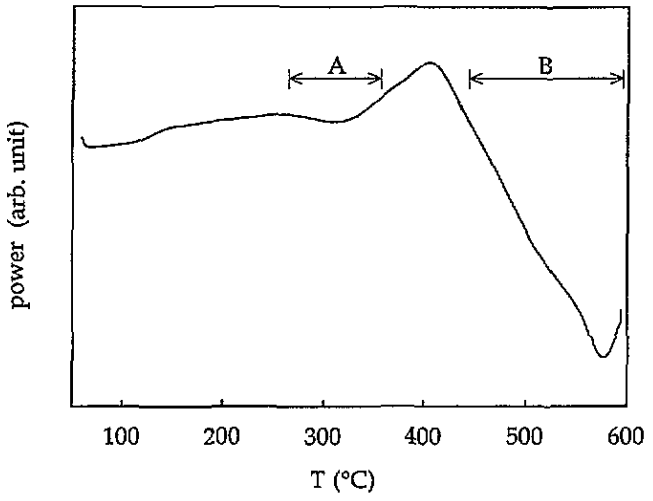

Figure 3. A differential scanning calorimeter plot for $Fe_{25}Cu_{75}$, as the temperature is ramped from 50 to 600 °C. The heating rate was 20 °C min^{-1}.

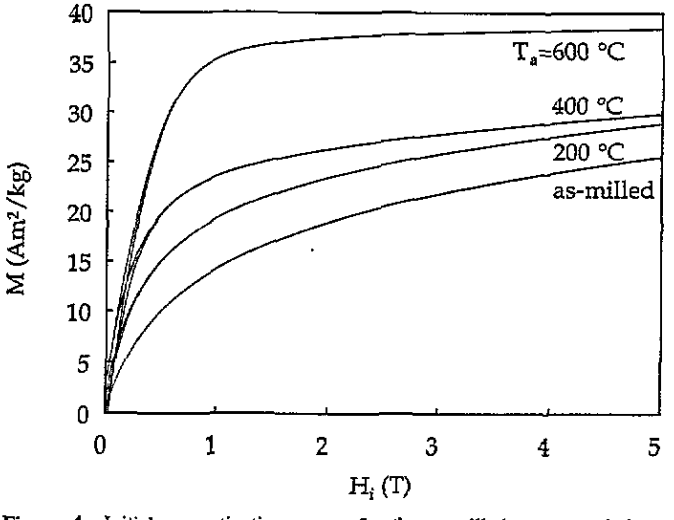

Figure 4. Initial magnetization curves for the as-milled and annealed samples, measured at room temperature.

12 T was 53.8 and 50.8 A m^2 kg^{-1} for temperatures of 40 and 100 K, respectively. These values, corresponding to 2.3–2.4 μ_B/Fe atom (as calculated for Fe dissolved in the FCC Cu phase) were close to the Fe-moment of 2.22 μ_B in the α-Fe phase [18] (assuming the Cu atoms do not carry a magnetic moment). These results show that the Fe atoms dissolved in the FCC Cu phase have a magnetic moment similar to that for the Fe atoms in the α-Fe phase, since the magnetic moment of the Fe in the FCC Cu phase could be slightly overestimated due to contamination by small amounts of Fe from the steel vial and balls used for the mechanical milling.

We have tentatively tried to analyse magnetization curves for the as-milled sample using the Langevin function [14], assuming there is a mixture of 7% Fe atoms in the α-Fe phase, 4% Fe atoms in γ-Fe phase and 89% Fe atoms dissolved in the FCC Cu phase. This latter we assumed to have a similar form to that of pure Fe clusters with a magnetic moment of 2.2 μ_B but containing no Cu. Using these assumptions then, magnetization curves taken for the as-milled sample at 350 and 400 K were fitted with a Langevin function. From the fitting parameters, an average Fe cluster size of 1 nm was obtained, assuming a spherical Fe cluster shape and ferromagnetic alignment within the clusters. The as-milled magnetization curves deviated from the Langevin function when measured at temperatures below 300 K, and the deviation increased with decreasing measuring temperature.

The Mössbauer spectrum taken at 77 K for the as-milled powder had a broadened distribution of hyperfine fields with an average hyperfine field of about 20 T, which is significantly lower than the hyperfine field expected for Fe-atoms having a magnetic moment of 2.3–2.4 μ_B (expected values are close to 33 T for the hyperfine field of α-Fe, having a moment of 2.22 μ_B). This behaviour can be explained by the superparamagnetism of inhomogeneously size-distributed Fe-rich regions in the FCC Cu phase [20].

The superparamagnetic properties discussed above indicate that Fe atoms dissolved in the FCC Cu matrix have an inhomogeneous distribution. The superparamagnetic behaviour may originate from regions of high Fe concentration in the FCC Cu matrix. The deviation from the Langevin function at measuring temperatures below 300 K may be due to the inhomogeneous distribution of the sizes of the Fe-dense regions, or due to interactions of these regions [21, 22]. These regions may contain Cu atoms which, along with surrounding Cu atoms can cause a non-vanishing anisotropy constant and in addition can cause non-uniform magnetic exchange interaction between Fe atoms.

Similar magnetization curves are reported for Co–Cu prepared by melt spinning [10] and Co–Au prepared by sputtering and mechanical alloying [11]. Superparamagnetism was found in these systems, and was due to small ferromagnetic clusters of Co embedded in the non-magnetic matrix (Cu, Au) [10, 11].

It can also be seen from figure 4 that magnetization increases with annealing temperature due to the formation of α-Fe. Powders annealed with $T_a \geqslant 400\,^{\circ}C$ have a low remanence and small coercivity (< 0.01 T), associated with magnetically soft α-Fe.

For powders annealed at 600 °C, the saturation magnetization was found to be 35–40 A m^2 kg^{-1}. This is less than the calculated magnetization obtained by assuming all the Fe atoms to be in the α-Fe phase (about 45 A m^2 kg^{-1}). This result agrees with Mössbauer measurements showing that a small amount of the Fe remains in the γ-Fe and Cu phases.

3.3. Magnetoresistance measurements

Magnetoresistance was measured for as-milled and annealed ($T_a = 200\,^{\circ}C$) cylindrical pellets, in magnetic fields of up to 12 T, and the resistance of these samples was found to decrease with increasing applied field (figure 5). These magnetoresistance curves for annealed and as-milled samples were similar in shape.

The resistance in zero field decreased with decreasing temperature (figure 5). A reduction of about 40% was measured at 50 K in comparison with that at 300 K. This result shows a large residual resistance component, probably due to a nanocrystalline structure with a high density of defects and grain boundaries.

A small but noticeable increase in the magnetoresistance effect was seen with decreasing measuring temperature for both samples (table 1), where the drop in resistance in fields of 12 T increased from 5.6% at 350 K to 7.3% at 50 K.

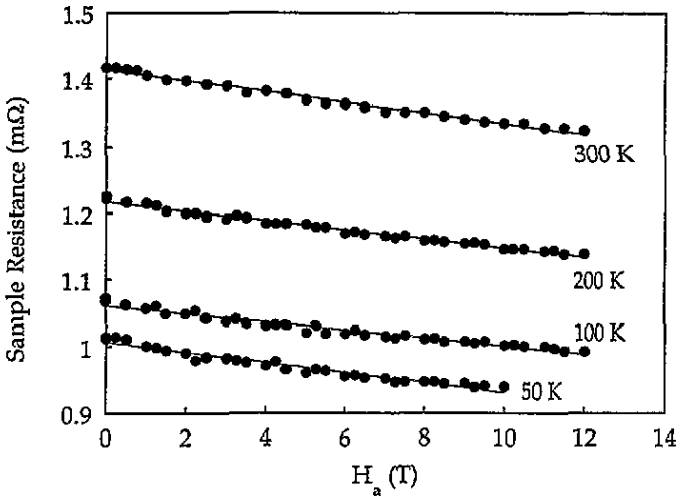

Figure 5. Sample resistance as a function of applied field for the as-milled sample.

Table 1. The magnetoresistance of the as-milled and annealed samples at measuring temperatures ranging from 50 K to 350 K. The maximum applied field was 12 T.

Temperature (K)	$[R(0) - R(12\ T)]/R(0)$ as-milled sample	$[R(0) - R(12\ T)]/R(0)$ annealed sample
350	5.64%	—
300	6.53%	—
290	—	6.31%
200	6.98%	6.80%
100	7.24%	7.55%
50	7.28%[a]	—

[a] Maximum field of 10 T.

No significant difference in the magnetoresistive effect was observed between the as-milled sample and the 200 °C annealed sample, when compared to the standard error.

This trend of increasing magnetoresistance with decreasing temperature is consistent with results obtained in other granular materials. For instance, mechanically alloyed Co–Ag shows a drop in resistance of 2.2% at room temperature, and 6.7% at 5 K [11]. Melt-spun $Cu_{90}Co_{10}$ shows a drop of 5% at 300 K, and more than 15% at 50 K [10].

This magnetoresistance effect is significantly larger than the 'ordinary' magnetoresistance (which is of the order of 1–2%). This may be due to interfacial scattering effects of regions of higher Fe density in the FCC Cu matrix, the mechanism of which would then be similar to that previously discussed [8, 9, 23].

4. Conclusion

The powder of starting composition $Fe_{25}Cu_{75}$ showed a single supersaturated FCC Cu phase in x-ray diffraction spectra after mechanical alloying. Annealing caused precipitation of γ-Fe (at temperatures of 300–400 °C) and α-Fe from Fe atoms present in the FCC Cu phase, and the amount of α-Fe increased with increasing annealing temperature.

Fe atoms dissolved in the FCC Cu matrix show a doublet in the Mössbauer spectrum at room temperature, but magnetization curves of this FCC Cu phase (which contains about 25 at.% Fe) could not be fitted with a paramagnetic curve. The magnetization curves taken at several temperatures between 50 and 400 K showed superparamagnetic behaviour. these results indicate that the Fe dissolved in the FCC Cu phase is possibly not homogeneously distributed, and forms nanoscale regions of higher Fe density in the Cu matrix.

A study of the magnetoresistive properties of mechanically alloyed $Fe_{25}Cu_{75}$ shows magnetoresistance in the as-milled and 200 °C annealed samples increasing slightly with measuring temperature, although there is no significant difference between the magnetoresistance of the as-milled and annealed samples if measured at the same temperature.

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