



An investigation of electrodeposited granular CuFe alloyed films

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Abstract

The thin-film alloy $Cu_x Fe_{1-x}$, with x = 0-0.60, has been produced by electrodeposition. X-ray measurements show that the film consists of a mixture of fcc Cu and bcc Fe. Mössbauer and SQUID measurements have been made on a range of concentrations.

1. Introduction

In recent years inhomogeneous granular films have become the subject of intensive investigations. This is due to the fact that these materials are of great interest from both fundamental and practical points of view. We consider that we are the first workers to use the relatively simple and cheap technique of electrodeposition to produce granular materials; in an earlier paper [1] we reported results for the $Cu_{1-x}Co_x$ system for x = 0.06 - 0.20. These samples were produced under conditions of constant current. An important feature of samples produced by electrodeposition is that they are inhomogeneous immediately after production, i.e. without the requirement of annealing. Furthermore, we have also observed a considerable GMR effect in these materials [2]. It therefore seemed relevant to us to continue these investigations in similar systems and we have, therefore, extended our investigations to the CuFe system, since this offers us both the opportunity to compare the behaviour of two similar systems, thus enabling us to gain further insight into the fundamental properties of these materials and also raises the possibility of producing even cheaper granular materials; a feature which is of considerable importance if their GMR properties are to be used, for example, in practical applications.

2. Experimental technique

 Cu_xFe_{1-x} films with x = 0-0.60 were electrolytically deposited from a solution with the following composition:

$FeSO_4 \cdot 7H_2O$	30.0 g/l
$Na_3C_6H_5O_7 \cdot 5.5H_2O$	120 g/l

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H ₃ BO ₃	6.6 g/l
$MgSO_4 \cdot 7H_2O$	23.3 g/l
$C_6H_4SO_2NHCO$	1.0 g/l
$CuSO_1 \cdot 5H_2O$	0-20 g/l

A current density of 5–60 mA cm⁻² was used at a temperature of 40°C and a pH of 6.0. Films were deposited onto three different types of substrates: Cu foil for SQUID measurements, ceramic wafer coated with a thin layer of NiP for GMR and X-ray measurements and onto Al foil for Mössbauer and TEM measurements. For the FeCu system, the current density plays a much more important role than in the electrodeposition of the CuCo system. The more CuSO₄ that there is in solution, the greater is the current density that must be employed in order to produce electrodeposition. This is why we do not have a linear increase of Cu in the films in proportion to the concentration of CuSO₄ in the electrolyte; for this reason it was easier to deposit Fe in the films than Cu.

X-ray measurements were made using a Dron-3M instrument with Co K α radiation with a graphite monochromator. The Mössbauer data were obtained using a constant acceleration velocity spectrometer calibrated using α -iron. The magnetic measurements were made using a Quantum Design (MPMS) SQUID magnetometer; temperatures could be controlled to within $\pm 10^{-2}$ K and fields could be set to an accuracy of $\pm 10^{-6}$ T.

3. Results and discussion

Fig. 1 shows schematically the results of the X-ray analysis of a range of film compositions obtained by varying the concentration of $CuSO_4$ in the electrolyte. We observe two lines corresponding to fcc Cu: a (111) line at $2\theta = 50.5^{\circ}$ and a (200) line at $2\theta = 59.2^{\circ}$, plus a further two lines for bcc Fe: a (110) line at $2\theta = 52.4^{\circ}$ and a (211)





Fig. 1. X-ray diagrams for the different CuFe films. The relative intensities of the lines are given in arbitrary units.

line at 99.4°. The (211) line for bcc Fe is absent from three of the spectra; we attribute this to a texturing effect which is typical for thin films. The peaks observed are seen to be generally shifted from the usual, tabulated positions of the pure elements to a smaller range of angles, which we interpret as being caused by a small increase of lattice parameter. This is partly due to the alloying with Cu, which has a slightly larger lattice parameter, and also to the fact that some of the other components of the electrolyte (e.g. Na₃C₆H₅O₇) are incorporated into the film during growth. With increasing Cu concentration in the electrolyte, and consequently in the film, a broadening of the X-ray peaks is observed. The width of the peak changes from 0.5°, for the lowest Cu concentration, up to a value of 1.3° for the highest concentration. This we assume is due to the presence of a range of particles of decreasing sizes. We thus conclude that the films consist of a mixture of fcc Cu and bcc Fe particles. These results are different than those for films produced by vapour deposition by Chien et al. [3] and by Sumiyama and Nakamura [4] using rf sputtering; those workers found a single-phase bcc structure up to a concentration of x = 0.30.

The Mössbauer results show remarkable changes in the spectrum as the Fe concentration is varied. At high Fe concentrations, the spectrum is predominantly sextet (magnetic) in nature exhibiting a nuclear magnetic hyperfine

Table 1

Mössbauer parameters obtained from the computer fits. The centre shifts (CS) are given relative to α -Fe. The percentage absorption area attributed to the non-magnetic component is also given

Cu conc., x	CS (para) (mm s ⁻¹)	CS (mag) (mm s ⁻¹)	H (kG)	Para (%)
0	0.19	0.02	333	1.42
0.13	0.15	0.03	327	3.75
0.25	0.21	0.02	332	4.35
0.35	0.31	0	0	100
0.42	0.21	0	0	100
0.60	0.18	0	0	100



Fig. 2. ⁵⁷ Fe Mössbauer absorption spectra for the Cu $_x$ Fe_{1-x} films with (A) x = 0, (B) x = 0.25, (C) x = 0.42. All measurements were at room temperature relative to a ⁵⁷CoRh source.

field of around 33.3 T but, as the Cu content increases, we observe the emergence of a second, non-magnetic phase in addition to the magnetic sextet (see Fig. 2). However, the magnetic hyperfine field for the sextet remains virtually unchanged from that for bulk Fe even up to 25% Cu addition. This is additional evidence for the fact that we are observing relatively pure bcc Fe particles in these granular materials. At room temperature, for Cu concentrations of 35% or greater, the magnetic sextet completely



Fig. 3. Magnetization curves for the Cu $_x$ Fe_{1-x} film with x = 0.42 measured at the indicated temperatures.

disappears and we are left with only a weak, non-magnetic central component. Table 1 lists the Mössbauer parameters obtained from the computer fits. It is interesting to note that our centre shift (CS) values obtained for the non-magnetic component are close to that quoted by Chien et al. [3] for dilute Fe in Cu (0.18 mm s⁻¹).

On the other hand, SQUID measurements show that at the above-mentioned concentrations of Fe, even when the magnetic sextet has disappeared, the samples still show a magnetic moment at room temperature (Fig. 3). This behaviour is difficult to explain at the preset time. In order to investigate this problem further, both low-temperature Mössbauer and SQUID measurements are in progress on samples with a wide range of compositions.

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References

- H.J. Blythe and V.M. Fedosyuk, Phys. Stat. Solidi (a) 146 (1994) K13.
- [2] V.M. Fedosyuk, O.I. Kasyutich and H.J. Blythe, to be published.
- [3] C.L. Chien, S.H. Liou, D. Kofalt, W. Yu and T. Egami, Phys. Rev. B 33 (1986) 3247.
- [4] K. Sumiyama and Y. Nakamura, J. Magn. Magn. Mater. 35