PRAMANA
— journal of
physics

Vol. 68, No. 1
January 2007
pp. 83–90

Giant magnetoresistance of electrodeposited Cu–Co–Ni alloy films

İ H KARAHAN*, Ö F BAKKALOĞLU† and M BEDIR†
*Department of Physics, Faculty of Kilis Science and Arts, University of Gaziantep, 79100 Kilis, Turkey
†Department of Engineering Physics, University of Gaziantep, 27310 Gaziantep, Turkey
*Corresponding author. E-mail: ikarahan@gantep.edu.tr

MS received 29 March 2006; revised 10 July 2006; accepted 11 September 2006

Abstract. Electrodeposition of CuCoNi alloys was performed in an acid–citrate medium. Nickel density parameter was varied in order to analyse its influence on the magnetoresistance. The structure and giant magneto- resistance (GMR) effect of CuCoNi alloys have been investigated. The maximum value for GMR ratio, at room temperature is 1% at a field of 12 kOe, and at 20 K is 2.1% at a field of 8.5 kOe for 3.1 Ni. The MR ratio of $Cu_{100-y-x}Co_yNi_x$ alloys first increases and then decreases monotonically with increasing Ni content. The GMR and its dependence on magnetic field and temperature were discussed.

Keywords. Magnetic films; electrodeposition; X-ray diffraction; magnetoresistance; magnetic measurement.

PACS Nos 75.70; 72.15.G; 81.15.L; 75.50.C

1. Introduction

Magnetoresistive materials have recently attracted attention due to their technological applications. The observation of giant magnetoresistance (GMR) in multilayers has again initiated magnetoresistance research on heterogeneous alloy films in the hope of detecting large magnetoresistance effect in these artificial systems. Different techniques have been used to produce heterogeneous alloys although the structure and therefore properties depend closely on the preparation techniques [1–4].

Electrodeposition, which is a relatively cheap technique, is an alternative method to other complex and sophisticated ones such as evaporation, sputtering, MBE, and it is also suitable for producing multilayer and immiscible metal combinations by control of the electrodeposition variables. Inhomogeneous CuCoNi alloy films are among the systems exhibiting GMR. In our previous paper [5], the GMR and the microstructure in $Cu_{1-x}Co_x$ (x = 0.06, 0.13, 0.17, 0.19, 0.21, and 0.26) granular films prepared by electrodeposition were reported. In order to improve GMR of Cu–Co systems, alloying addition such as Cr, Fe, Mn and Ni have been tried [6–9].

Among these elements, only Ni addition gives a prospect with an improved GMR ratio, however the reason for this remains unclear. The phase segregation in Co–Ni–Cu films is not a pure nucleation decomposition or growth process. It is closely connected with the Ni content. In particular, in Co–Ni–Cu granular films with low Ni content, the magnetoresistance ratio is larger than in Co–Cu granular films.

In this paper, the crystal structure, electrical conduction and magnetic properties of $Cu_{100-y-x}Co_yNi_x$ (x = 1.6, 2.2, 2.6, 3.1, 4.1, 5, 5.5, 6.6, 11.5) alloy films produced by electrodeposition and the effect of Ni addition on the GMR properties is investigated.

2. Experimental details

Electrodeposition of Cu–Co–Ni films was carried out at a constant current density from an aqueous electrolyte of sulfates of Cu, Co and Ni. The electrolytic bath was composed of $CuSO_4{\cdot}7H_2O$, $CoCl_2{\cdot}6H_2O$, $NiSO_4{\cdot}6H_2O$, H_3BO_3, $MgSO_4{\cdot}7H_2O$, $CoSO_4{\cdot}7H_2O$ and $Na_3C_6H_5O_7{\cdot}2H_2O$. The substrates for the electrodeposition were aluminum which was subsequently stripped from the films using 10% NaOH solution. The deposition was performed with a current density of 5 mA/cm^2 at room temperature. A two-electrode composition was used: platinum as anode and aluminum as cathode. The compositions of the films were determined using both an energy dispersive spectrophotometer and an atomic absorption spectrophotometer. The crystallographic structures of the as-deposited films were studied by X-ray difractometer (Rigaku-2200 D/max corp., Japan) using CuK_α radiation. The resistivity measurements were determined using the usual four-point probe method in an applied field of ±8.5 kOe using a Varian V-2900 electromagnet for the temperature-dependant investigation. A current of 0.1 mA was kept constant, and directed to the same direction of the magnetic field parallel to the film plane. A helium cryostat (Leybold RW2 closed helium cryostat) was used to control the temperature variation with a sensitivity of ±0.2 K. The dimensions of the samples for the resistivity measurements were 4 mm × 4 mm. The magnetic field-MR measurements were carried out in an alternating magnetic field as 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 at room temperature. The temperature-depended MR measurements were carried out in ±8.5 kOe at 20 to 320 K.

3. Results and discussion

3.1 *Sample characterization*

According to Vegard's rule, the lattice parameter is proportional to the atomic per cent of solute present in continuous solid solution alloys [10]. Figure 1 shows an example of the diffraction spectra of the electrodeposited $Cu_{73}Co_{22}Ni_5$ alloy film. The diffraction patterns were taken from different parts of each film to check the distributions of constituents in the film and no difference in the spectra from the different parts of each film was detected.

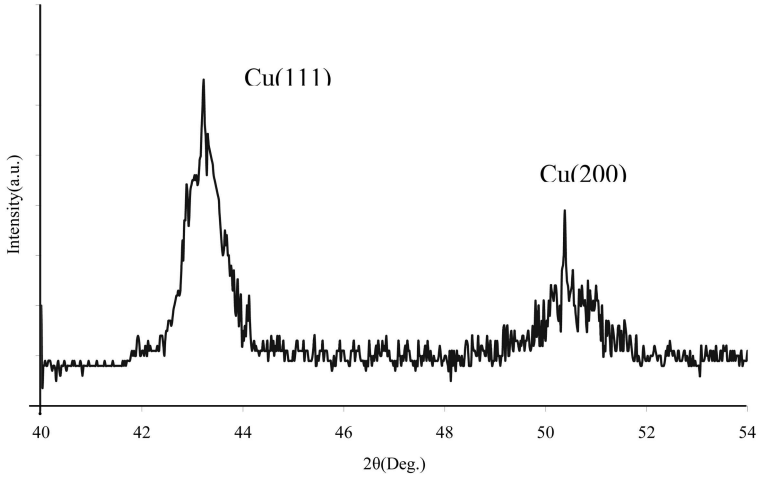

Figure 1. X-ray diffraction spectrum of electrodeposited $Cu_{73}Co_{21}Ni_5$ alloy film.

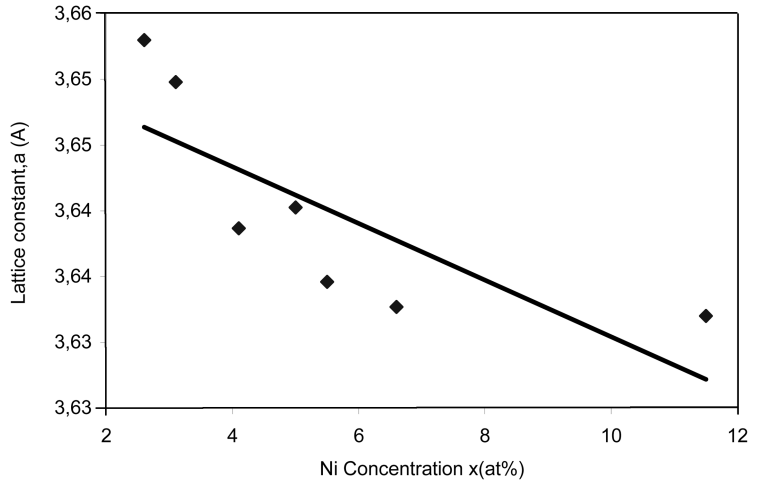

Figure 2. Variation of lattice constant a, which is determined from fcc diffraction.

Both lines in the diffraction spectrum of CuCoNi alloy films correspond to the fcc Cu structure. The lines observed in the spectra of all the films were almost identical, although the Cu diffraction lines are shifted toward higher angles with increasing Co content in the film. The lattice parameters were calculated from the diffraction angles of the fcc Cu(1 1 1) line. As can be seen from figure 2, the lattice parameters reduce linearly obeying Vegard's rule as the nickel content in the films increases. The alloy films prepared in this work may therefore be regarded as solid solutions.

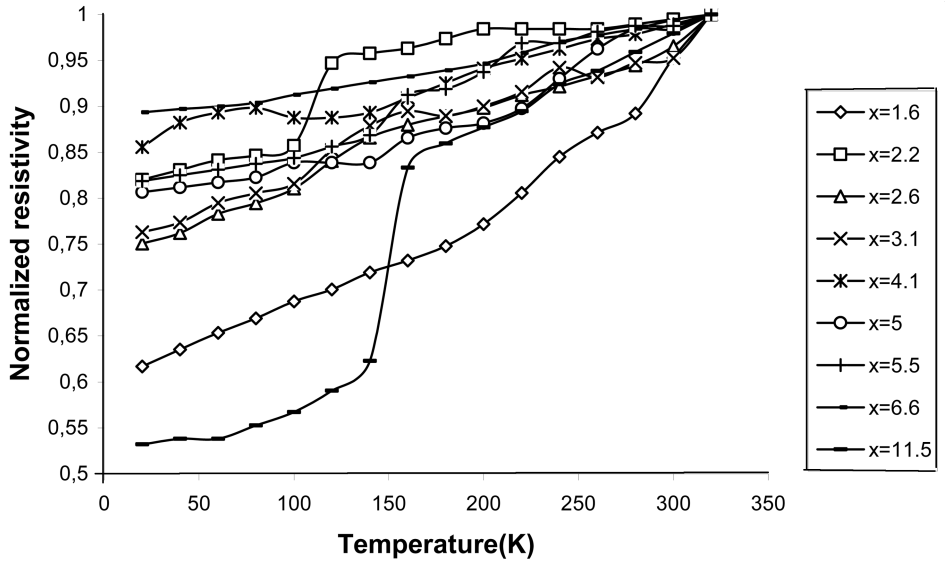

Figure 3. Normalized resistivity curves as a function of temperature.

3.2 *Resistivity and magnetoresistance measurements*

Resistivities were measured using the standard four-point probe method. The thermal voltage effect was eliminated by taking the average of voltage readings with two reverse currents and magnetic fields at each temperature. Each sample was measured several times to make sure the data obtained was reliable. Figure 3 shows the temperature versus normalized resistivity values of the films.

A linear change in the resistivity of CuCoNi film with the variation of the Ni content from $x = 1.6$ to 11.5 could not be observed although the change in the resistivity with the variation of temperature is almost linear for all the five samples except for the $x = 11.5$ and 1.6 films. The biggest resistivity was detected in the $x = 3.1$ film while the largest change in resistivity with temperature was observed in the $x = 11.5$ film which has the second lowest resistivity at 20 K and shows a very sharp resistivity increase above 140 K. The temperature-dependent resistivity curves in the figure appear not to obey Matthiessen's rule which predicts parallel temperature-dependent resistivity curves. However, the Kondo effect predicts a departure from the Matthiessen's rule in samples with small magnetic atom contamination, e.g. Co or Ni, in a non-magnetic metallic matrix, e.g. Cu. This anomalous behavior is due to an additional scattering of electrons by magnetic moments on the impurity centers [11]. The resistivity temperature variation with Co content may therefore be much more complex than that implied by Matthiessen's rule. However, the decrease in resistivity with decreasing temperature seems to be due to the reduction of the numbers of both phonons and magnons. The decrease in the number of magnons may be determined by measuring the magnetoresistance effect with decreasing temperature. The random variation in electrical values results from electrochemical film composition variation. However although Ni contents

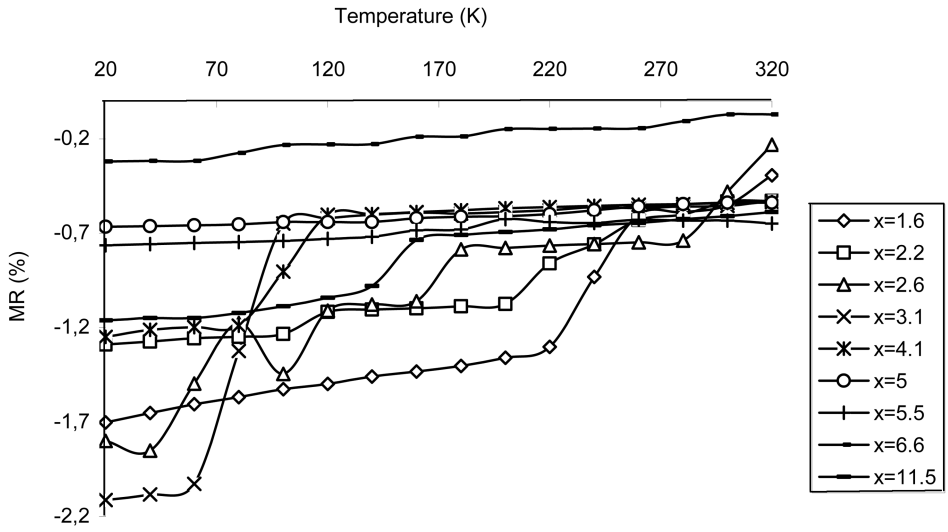

Figure 4. Variation of magnetoresistance (MR) ratio of electrodeposited CuCoNi samples with temperature.

changed against fixed amount of Cu and Co in electrolyte, all the components of those of three metals appeared to be in the film changed during electrochemical treatment. Because of that random changes have been observed.

The magnetoresistance (MR) ratio in this study is defined as $(R(0) - R(H = 8.5 \text{ kOe}))/R(H = 8.5 \text{ kOe})$ where $R(H = 8.5 \text{ kOe})$ is the resistance of sample measured under the applied magnetic field of 8.5 kOe and $R(0)$ is the resistance when no magnetic field is applied. The giant magnetoresistance (GMR) ratio means a MR ratio bigger than 1% [3]. Magnetoresistance was measured by applying the magnetic field and current parallel to the film plane and subsequently checked by applying the magnetic field perpendicular to the current and parallel to the film plane. Both measurements showed a negative magnetoresistance effect and any difference between them could not be detected. Figure 4 shows the temperature variation of the MR ratios of all samples. At 320 K, all samples have MR value below 1%. The MR values at 320 K change order at 20 K, because the variation of the MR ratio with decrease in temperature is different for each sample. At 20 K, the samples of $x = 1.6$, 2.2, 2.6, 3.1, 4.1 and 11.5 reach MR ratios higher than 1%, i.e. clearly a GMR effect. The increase in the MR ratio with decreasing temperature may represent the reduction in spin-magnon scattering at lower temperatures i.e. represents the relative reduction in the number of magnons.

Figures 5 and 6 represent Ni concentration dependence of the MR ratio, MR at 20 K and RT of CuCoNi alloys respectively. When the Ni content increases, the MR ratio first increases and then decreases. The present results are in agreement with those in the Co–Ni–Cu granular ribbons. A 5 at.% Ni-addition can improve GMR of the melt-spun and liquid quenched Co–Cu alloy [12–14], due to which Ni can inhibit the liquid phase separation at high temperatures and increase the density of fine magnetic Co-precipitates [15]. Figure 7 shows the MR ratio at room

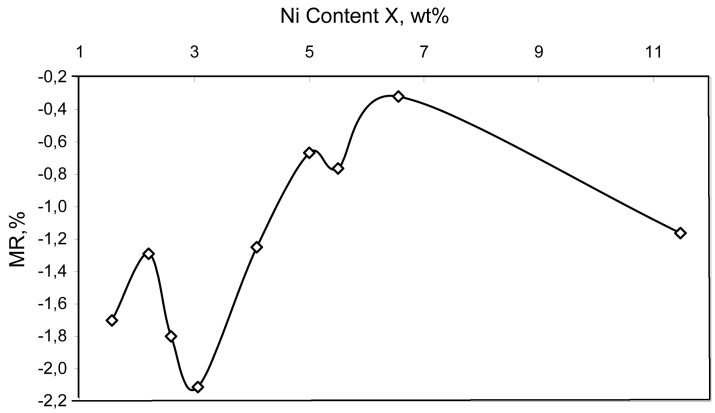

Figure 5. Ni concentration dependence of MR ratio at 20 K and 8.5 kOe of CuCoNi alloys.

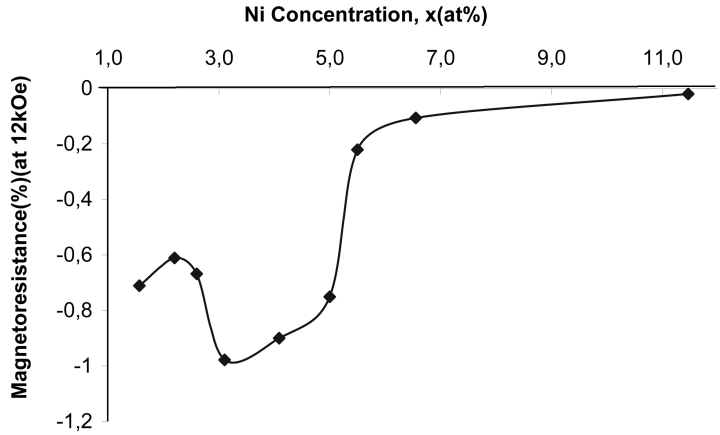

Figure 6. Ni concentration dependence of MR ratio at room temperature and at 12 kOe magnetic field of CuCoNi alloys.

temperature as a function of the applied magnetic field for $Cu_{71.9}Co_{25}Ni_{3.1}$ alloy film. With increasing magnetic field, the electrical resistivity of alloys decreases monotically with increasing magnetic field. All samples show similar results. The MR curve in figure 7 consists of a rapid drop in the MR at low fields that originates from the interplay between spin-dependent scattering phenomena in neighboring magnetic grains, followed by a long tail at rather high fields [16].

3.3 *Bath composition*

Different concentrations of Ni (1, 5, 10, 15, 20, 25, 30, 35, 40 at.%) in the electrolyte with fixed amount of Cu and Co were taken to obtain different bath compositions.

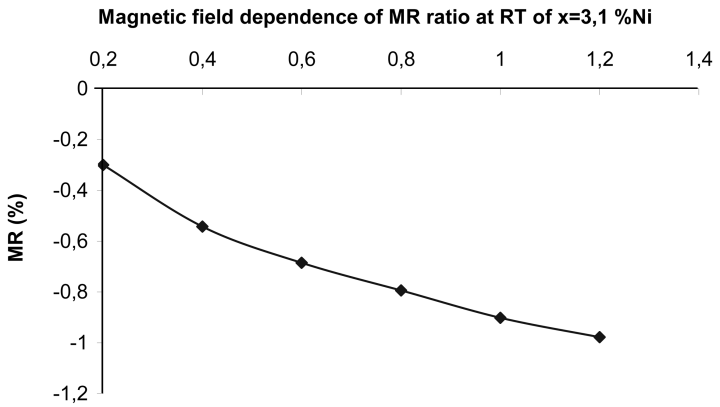

Figure 7. Magnetic field dependence of MR ratio at RT of $Cu_{72}Co_{25}Ni_3$.

The electrolyte was not stirred. The films were deposited at a current density of 5 mA/cm^2 at room temperature. The pH of all the baths was 6.0. AAS studies revealed that the Co concentrations in the films deposited from baths containing 1, 5, 10, 15, 20, 25, 30, 35, and 40 g/l Ni are 1.6, 2.2, 2.6, 3.1, 4.1, 5, 5.5, 6.6 and 11.5 at.%, respectively. As the Ni concentration (in the bath) is increased from 1 to 5 at.% the MR of the film increases. Further increase in the Ni concentration decreases the MR of the film. It is thus noted that the change in bath composition results in the change in the film composition, which in turn affects the MR. The low MR values for films can be explained with the relatively dilute magnetic concentration leading to fewer magnetic–non-magnetic interfacial scattering sites.

4. Conclusions

The electrodeposited CuCoNi films were prepared as a solid solution of Cu, Co and Ni. The resistivity change with temperature in the electrodeposited CuCoNi alloy films does not obey Matthiessen's rule. GMR effects of 1.7, 1.3, 1.8, 2.1, 1.3 and 1.2% are observed in $x = 1.6$, 2.2, 2.6, 3.1, 4.1 and 11.5 alloy films, respectively, although $x = 5$, 5.5 and 6.6 films show a MR effect under 1% at 20 K. It is evident that electrodeposition is an appropriate technique for the preparation of the GMR thin films. Various deposition parameters affect the GMR of the film largely via compositional and nanostructural changes. MR strongly depends upon the magnetic Co and Ni concentration in the films. Many of the process parameters also influence the film microstructure, thereby affecting the GMR.

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