

The pH Dependence of Magnetoresistance in Cu-Co Alloy Films Formed by Electrodeposition

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Thin films of $\text{Cu}_{1-x}\text{Co}_x$ were electrochemically deposited onto aluminum substrates in a single sulfate bath. The GMR effect was investigated in the temperature range 20 to 300 K and in the magnetic field range 0 to 12 kOe. The bath pH values were selected as 5.25, 5.5, 5.75, 6, and 6.25. The compositions of the electrodeposited $\text{Cu}_{1-x}\text{Co}_x$ films were determined to be $x = 27.7, 27.4, 28.5, 37.9,$ and $28.4,$ respectively, by an atomic absorption spectrometer and an energy dispersive X-ray spectrometer. The crystal structure was FCC-Cu for all films, but a shift in the direction lines was observed with increasing Co content. All films showed a negative magnetoresistance (MR) effect. The maximum MR ratio at a magnetic field of 8.5 kOe was 1% in the pH=6 film at room temperature and 3.3% in the pH=6 film at 20 K. It was found that the composition, structure, and magnetoresistive (GMR) behaviour of the thin films exhibit a strong dependence on the pH values of the bath electrolyte.

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I. INTRODUCTION

Very intensive attention is now focused on magnetoresistive granular alloy films by researchers and technologists. The main reason for this is due to the existence of their GMR. In the presence of a magnetic field, magnetoresistive materials can exhibit a large drop in resistivity, this is the so-called giant magnetoresistance (GMR) effect [1, 2]. Heterogeneous alloy films are immiscible combinations usually prepared by electrodeposition [3–12]. In heterogeneous systems the ferromagnetic grains are distributed within a nonmagnetic matrix, whereas the GMR effect mainly originates from a spin-dependent scattering of the conduction electrons at the interface of the ferromagnetic (FM) particles [13]. Cu-Co alloy is a typical heterogeneous alloy showing GMR. This system is immiscible at room temperature, and the formation of a supersaturated Cu-Co phase is possible [14]. In the equilibrium state the solid solubility between Cu and Co is negligible at room temperature, and Co and Cu do not form solid solutions with a wide composition range. The film structure and properties are dependent closely on the preparation techniques [15–18]. The relationships between the production conditions and the magnetoresistive properties of the films are as yet unclear.

Electrodeposition is a cheap, relatively simple, and effective method of producing metastable alloy films. Moreover, electrodeposition is also an alternative to other more

complex and sophisticated techniques. Efficient control of the processing parameters has made it possible to prepare metallic nanostructures of a quality comparable with those prepared by physical vapor deposition [19]. The bath pH is only one of the suitable choices among the various electrodeposition process parameters which could be used to control the microstructure of the film and the volume fraction of the ferromagnetic metal in the film, thereby optimizing the magnetoresistance.

In this paper, our aim is to investigate the influence of the effect of pH on the crystal structure, electrical conduction, and magnetoresistance properties of electrodeposited CuCo heterogeneous alloy films.

II. EXPERIMENTAL DETAILS

The electrodeposition experiments were carried out using 1 cm² aluminum foil substrates, which had been degreased with 1 M sodium hydroxide followed by deionized water cleaning. The Al substrates were first mechanically and then electrochemically polished. All films were stripped from their substrates in a NaOH solution. The electrodeposition bath consisted of CuSO₄·7H₂O, CoCl₂·6H₂O, H₃BO₃, MgSO₄·7H₂O, CoSO₄·7H₂O, and Na₃C₆H₅O₇·2H₂O. The bath solution was freshly prepared before each deposition. The deposition was performed at room temperature with a current density of 5mA/cm². A two-electrode composition was used, with platinum as the anode and aluminum as the cathode. To study the effect of the pH of the electrolyte on the magnetoresistive behavior of the deposited Cu–Co films, the pH of an electrolyte containing 35 at. % Co was varied in the range 5.25–6.25 using NaOH, and a set of five different Cu_{1-x}Co_x alloy films were obtained.

The compositions of the films were determined to be $x = 27.7, 27.4, 28.5, 37.9,$ and 28.4 for the pH values of 5.25, 5.5, 5.75, 6, and 6.25, respectively, found using both an energy dispersive spectrophotometer and an atomic absorption spectrophotometer and taking their average. The thicknesses of the films were determined to be 2.18, 2.13, 2.24, 2.52, and 2.24 μm for the pH values of 5.25, 5.5, 5.75, 6, and 6.25, respectively. The crystallographic structures of the as-deposited films were studied by an X-ray diffractometer (Rigaku-2200 D/max corp., Japan) using CuK α radiation. The surface structures of the films were determined by a scanning electron microscope (SEM-Jeol 6400). The resistivity measurements were performed using the usual four-point probe method in an applied field of ± 8.5 kOe using a Varian V-2900 electromagnet. A constant current of 0.1 mA was applied and directed to the same direction with 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 \times 4 mm.

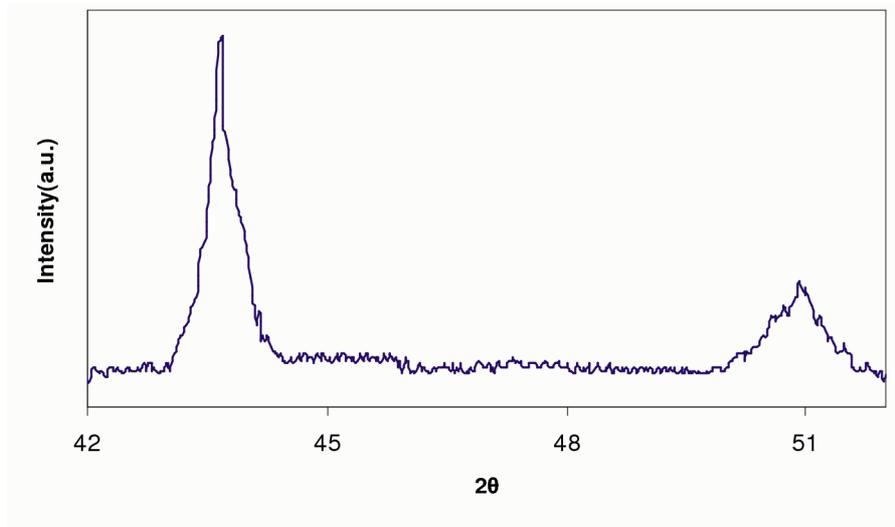


FIG. 1: X-ray diffraction spectrum of pH= 6 CuCo alloy film at room temperature.

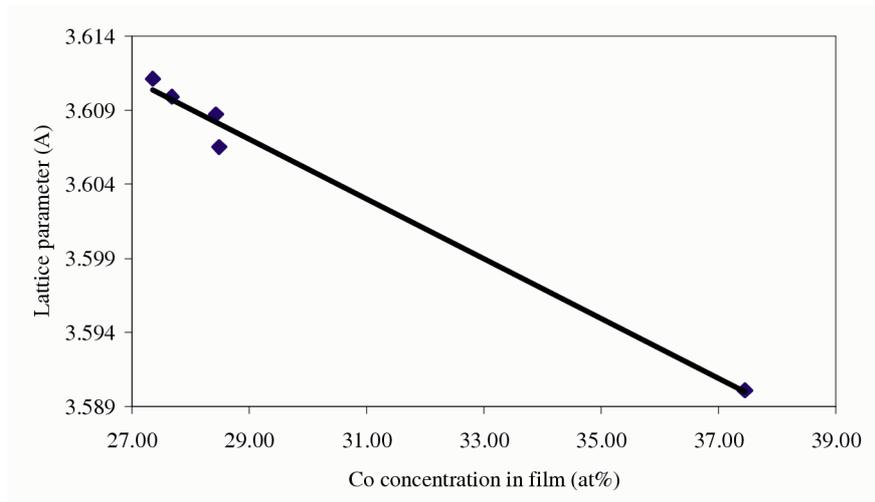


FIG. 2: Variation of the lattice constant a , which is determined from the FCC diffraction angles.

III. RESULTS AND DISCUSSION

Fig. 1 shows the X-Ray diffraction spectra of a pH=6 CuCo film. Both peaks in the diffraction spectrum of the $\text{Cu}_{1-x}\text{Co}_x$ alloy films correspond to the FCC-Cu structure. The diffraction peaks obtained indicate the pure Cu-FCC (111) and (200) planes. According to Vegard's rule, the lattice parameter is proportional to the atomic percent of solute present in continuous solid solution alloys [20]. The lattice constants of the CuCo films determined from the X-ray diffraction angle are plotted against the Co concentration of

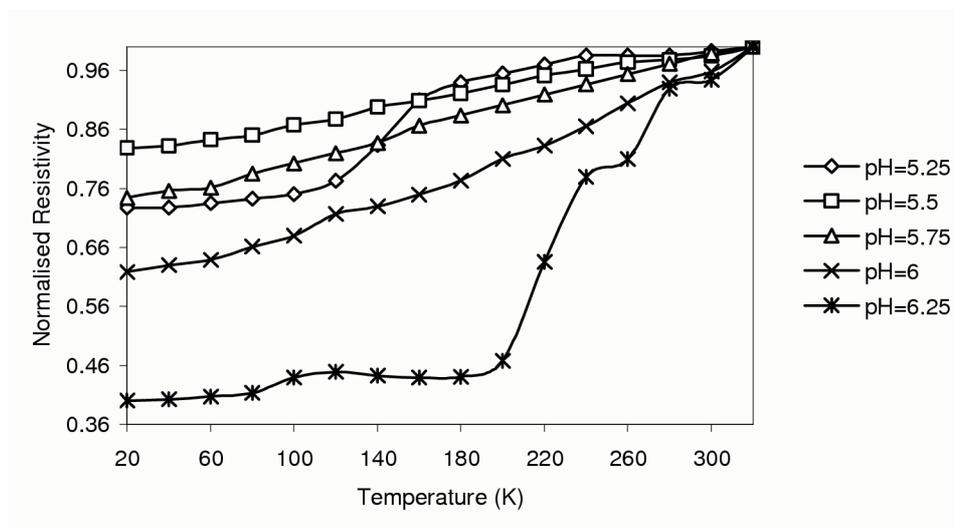


FIG. 3: Normalized resistivity curves of CuCo alloy film as a function of temperature.

the film in Fig. 2. The lattice constants of the films decrease linearly with increasing Co concentration, which is an indication of Vegard's law. This showed that the CuCo alloy films form a solid solution. The resistivity and magnetoresistivity measurements were obtained using the usual four-point probe method. The thermal voltage effect was eliminated by taking the average of the voltage readings with two reverse currents and magnetic fields at each temperature. Each sample was measured several times to make sure that the data obtained was reliable. Fig. 3 shows the temperature versus normalized resistivity values of the films. A linear change in the resistivity of the $\text{Cu}_{1-x}\text{Co}_x$ films with a variation of the pH from 5.25 to 6.25 could not be observed. The biggest resistivity was detected in the $\text{Cu}_{72.6}\text{Co}_{27.4}$ (pH=5.5) film. 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 rule in samples with small magnetic atom contamination, e.g., Co or Fe, 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 [21]. The decrease in the 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.

Two kinds of MR measurements were carried out. The first one was defined as a function of temperature and the other one was a function of magnetic field. The temperature dependent magnetoresistance ratio in this study is defined as $(R(H=8.5 \text{ kOe}) - R(H=0))/R(H=0)$, where $R(H=8.5 \text{ kOe})$ is the resistance of the sample measured under the applied magnetic field of 8.5 kOe, and $R(0)$ is the resistance without applying a magnetic field. The magnetic field dependent MR ratio is defined as $(R(H=12 \text{ kOe}) - R(H=0))/R(H=0)$. The giant magnetoresistance ratio means a MR ratio larger than 1%.

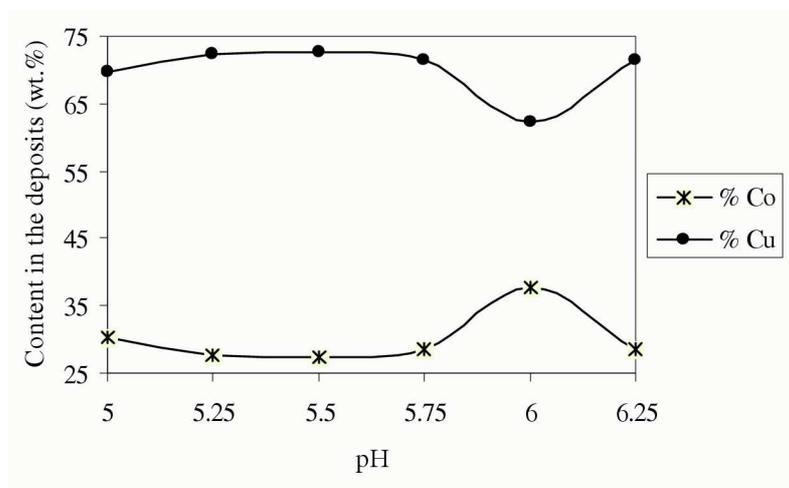


FIG. 4: Variation of Co and Cu concentration of CuCo samples with pH values.

The 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. This can be explained by the fact that the maximum applied field was 12 kOe, which is too small to be able to detect such differences. The saturation field for granular magnetic materials is rather large (in some cases above 150 kOe), and this defines the region where these differences could be seen.

The pH value is an important factor affecting film composition. The Co concentration in thin films depends on the electrodeposition current density and the bath pH [22]. As the pH increases from 5.5 to 6.0 the cathode potential increases, and hence more cobalt gets electrodeposited in the film. A further increase in pH to 6.25 results in the decrease in the Co content in the film and leads to a deterioration in the physical properties. The same deteriorations were observed under pH=2.5. As a result of the change of the magnetic Co component in the film, the GMR was affected. Fig. 4 shows how the Co and Cu concentrations in the film change with the value of the electrolyte pH.

An example of the SEM photographs of the electrodeposited CuCo films is presented in Fig. 5. This photograph of the film shows that our CuCo alloy films have a granular structure.

Fig. 6 presents the variation of the GMR with the bath pH values at room temperature and 20 K. Increasing the pH value first increased the GMR, and a peak appears at pH=5.5 at room temperature and at pH=5.25 at 20 K, then a decrease occurred with increasing pH. Above pH=5.75, the GMR again increased at 20 K up to 3.03% at pH=6.25. The observed variation in the MR with the variation of the pH value in granular alloys can be explained by the electron scattering from grain boundaries. In our films, the pH changed the composition and grain structures, which caused the observation of different GMR values

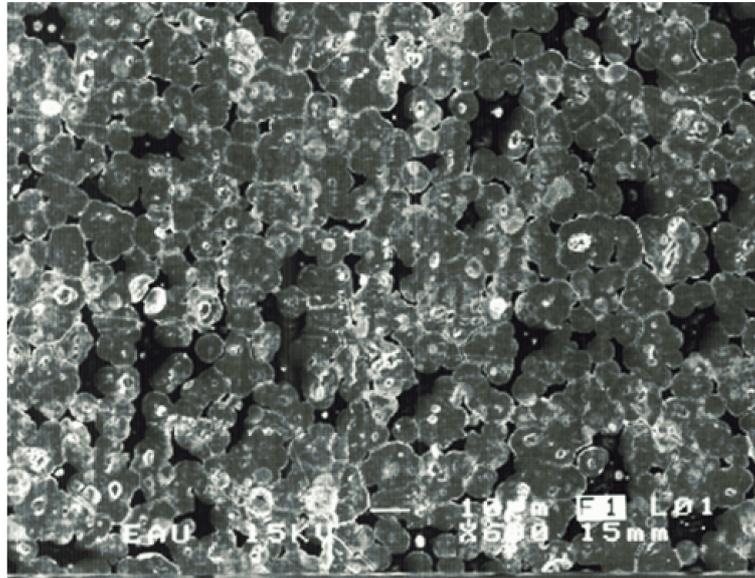


FIG. 5: Scanning electron microscopy film of pH=5 CuCo film.

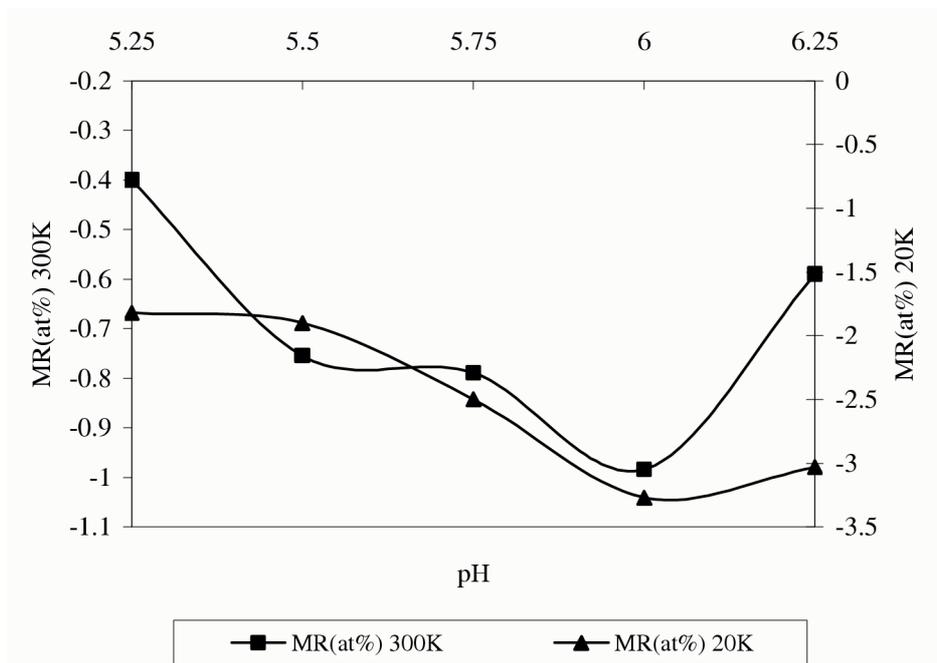


FIG. 6: Variation of magnetoresistance (MR) ratio of CuCo alloy films with pH values at different temperatures.

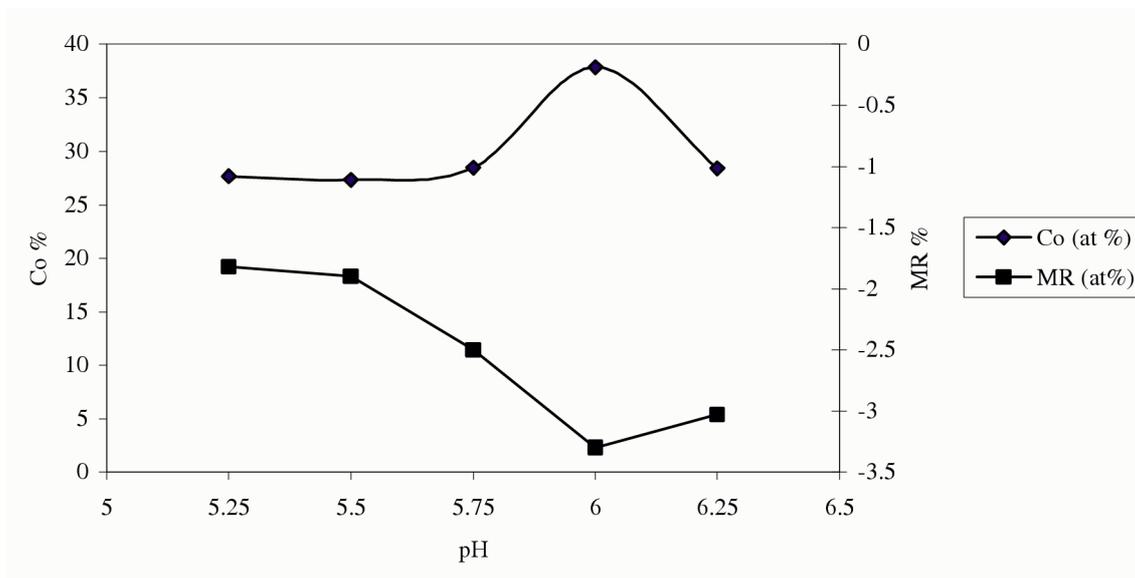


FIG. 7: Variation of magnetoresistance (MR) ratio and Co content of CuCo alloy films with pH values.

in the films with different composition and structure.

In Fig. 7 the variation of the magnetoresistance (MR) ratio and Co content of CuCo alloy films with pH values can be seen. We can understand from this figure that increasing the pH increased the MR ratio until pH= 6, then it decreased depending on the Co content.

The grain size was analyzed by Scherrer's formula [23] to be between 60–39 nm. It reduced with increasing pH value. The XRD analysis shows that the grain size reduces with increasing pH value, this explains the decrease in the coercivity.

IV. CONCLUSION

The CuCo alloys produced by electrodeposition are solid solutions, and these as-deposited samples exhibit the GMR effect. The resistivity variation with temperature in the electrodeposited CuCo alloy films did not obey Mattheissen's rule. The variation in the pH values changes the MR ratio, because of the change in the film composition as well as its grain structure. The MR ratios were examined against both temperature and the magnetic field. For the electrodeposited CuCo films, the value of the MR ratio of 0.08%, which is the lowest value at 0.85 T among the films studied at room temperature, jumped to 3% for the same field at 20K. The change in the MR ratio as a function of temperature is directly related to the change in the number of magnons. As the temperature decreases the number of magnons decreases. The highest decrease in the number of magnons therefore seems to be in the film obtained at pH=6.25. As can be seen from Figure 6, the MR ratio of the CuCo film at 20K first increases with an increasing Co content from $x = 27.4$ to 37.9. The

highest value of the GMR appears at $x = 37.9$. When the composition of Co in the film is low, the number of magnetic grains is small; then the lack of magnetic scattering centers surely leads to the small value of the GMR. With increasing Co concentration, the number and size of the grains increase, so the GMR tends to rise. With the further increase of Co concentration, GMR decreases. This behavior can be explained as follows: with increasing Co concentration, a magnetic percolation threshold is reached so that neighboring grains become strongly ferromagnetically coupled. Long before the actual Co percolation, a large ferromagnetic domain has formed; this makes the main contribution to the drop of the GMR at large Co concentration. In all the samples the MR values at room temperature increase with increasing magnetic field. The bath pH value affects the concentrations of the copper and cobalt and the grain sizes, and therefore the number of magnetic scattering centers.

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