

Comparison of Ni–Cu alloy films electrodeposited at low and high pH levels

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Abstract

Ni–Cu alloy films were potentiostatically electrodeposited from the electrolytes with low pH (2.0) and high pH (3.3) levels. The structural analysis of the films was carried out using the X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The XRD data showed that the crystal texture degree was different for the films grown at high pH and low pH. At high pH, the films have a strong (1 0 0) texture of the face-centred cubic (fcc) structure, while for the films at low pH the crystal planes are randomly oriented, as in a powder pattern of Cu (or Ni). The SEM studies revealed that the surface morphology of the films strongly depend on the electrolyte pH. Furthermore, the magnetic characteristics studied by a vibrating sample magnetometer (VSM) and magnetotransport properties were observed to be affected by the electrolyte pH. The differences observed in the magnetic and magnetotransport properties were attributed to the structural changes caused by the electrolyte pH.

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1. Introduction

Thin films with ferromagnetic components such as Fe, Ni and Co have attracted much interest for a long time, due to their potential applications such as magnetoresistive sensors and data storage devices. Single ferromagnetic films such as Ni, Fe Co and their alloys exhibit anisotropic magnetoresistance (AMR) [1,2], while heterogeneous alloy films such as Co–Cu exhibit giant magnetoresistance (GMR) [3]. Both AMR and GMR are of considerable importance from scientific and technological points of view, due to the use in devices such as magnetic recording heads and magnetic sensors.

Today, in order to fabricate metallic films, there are many deposition techniques with vacuum (sputtering and molecular beam epitaxy) and non-vacuum (electrodeposition). Among them, the electrodeposition is an excellent and inexpensive tool to produce materials from thick metal deposits with a very large surface area to ultra thin metal films with a few nanometer

sizes. In electrodeposition process, the film properties can usually change on depending on deposition conditions, e.g., current density, deposition potential, bath type and electrolyte pH. By adjusting the electrochemical deposition conditions as well as physical parameters such as thickness, the substrate type and orientation, it can be possible to control and optimise the structural, mechanical, magnetic and magnetotransport properties of electrodeposited films. In particularly, in electrodeposited films, the electrolyte pH has been reported to play an effective role on crystal size [4] and GMR [5].

Ni–Cu system is one of the most studied topics as both single and multilayered films. When Ni is alloyed with Cu, it is possible to grow strain free films, because they have identical crystal structure (face centred cubic) and almost the same lattice parameters (approximately 2.5% misfit). Ni–Cu alloys find applications such as corrosion resistance and decoration in industrial area. In this work, the structural, magnetic and magnetotransport properties of Ni–Cu films grown at high pH (3.3) and low pH (2.0) were investigated. It was observed that the surface morphologies and textures of the films are affected considerably by the electrolyte pH. Also, the magnetic and magnetotransport properties change with the electrolyte pH.

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2. Experimental

Two separate electrolytes consisting of 2.0 M nickel sulphamate and 0.5 M boric acid were firstly prepared. The pH of the freshly made electrolytes was 3.3. First group Ni–Cu films were produced from the electrolyte with pH 3.3. The pH value of the second electrolyte was first deliberately reduced by Ni deposition using an inert anode, until its pH value became 2.0 (the decrease in the bulk Ni concentration caused by this procedure is insignificant) and then 0.04 M copper sulphate was added. Second group Ni–Cu films were grown from this electrolyte with the pH 2.0.

Films were deposited in a cell with three electrodes using an EG&G Potentiostat/Galvanostat (model 362) controlled by a personal computer with our own software. Polycrystalline Ti sheets served as substrates. Prior to deposition, one face of the substrate was first polished mechanically by emery paper and then covered by electroplating tape, except for an area of $\sim 2.9 \text{ cm}^2$ for deposition. Subsequently, the substrate was washed in 10% sulphuric acid and distilled water successively. The counter electrode (anode) was a platinum foil with an area larger than the exposed area of the substrate. A saturated calomel electrode (SCE) was used as the reference electrode. All Ni–Cu films were deposited at room temperature using a cathode potential of -1.7 V with respect to the SCE and their nominal thickness was fixed at $2 \mu\text{m}$. After the deposition is completed, the films were mechanically peeled off their substrates and then mounted on glass.

The structural analysis of the films was made using X-ray diffraction (XRD) with Cu K α radiation (0.15406 nm) in the range $2\theta = 40\text{--}80^\circ$ with a step of $\Delta(2\theta) = 0.02^\circ$ and the surface morphology by a scanning electron microscopy (SEM). The film composition was determined using an X-ray energy dispersive (EDX) spectrometer in the SEM. Magnetoresistance (MR) measurements were carried out at room temperature using the Van der Pauw (VDP) geometry with four point probes arranged in a square. Electrical contact was made on the corners of the square film by means of four spring-loaded point probes. The potential difference between two probes on one side of the square was measured while the current was flowing through other probes on the opposite side, as described in previous work [6,7]. The magnetic field applied in the film plane was changed up to $\pm 10 \text{ kOe}$. The field was applied both parallel and perpendicular to the current flowing in the film plane to measure the longitudinal and transverse magnetoresistance, respectively. Magnetic characteristics of the films were determined by a vibrating sample magnetometer (VSM).

3. Results and discussion

X-ray diffraction measurements were made on Ni–Cu films grown at two different pH levels. Fig. 1(a) and (b) show the XRD patterns of Ni–Cu films produced at high pH 3.3 and low pH 2.0, respectively. As seen from the XRD patterns, the reflections from three characteristic crystal planes, $\{111\}$, $\{200\}$ and $\{220\}$, of the face-centred cubic (fcc) structure clearly appear at $2\theta \cong 44^\circ$, 51° and 76° , respectively. For cubic structures, since $\sin^2\theta$ values of the peaks linearly vary with the sum of squares of their Miller indices, these data was fitted to a straight line using the least squares technique [8]. Using the slopes of the obtained lines, the lattice parameters were found to be $0.3523 \pm 0.0009 \text{ nm}$ for the sample at grown high pH and $0.3519 \pm 0.0006 \text{ nm}$ for that at low pH. The errors in the lattice parameters are the standard errors, which were determined from the standard deviations in the slope. XRD data showed that Ni–Cu films formed a solid solution based on only the fcc phase at each pH level under study. The lattice parameter of the films deposited at high pH is slightly larger than that of the films at low pH, due to probably the more Cu content of the films at high pH, (see EDX data in Table 1). As the Cu content increase the lattice parameter of the Ni–Cu films is expected to increase since the lattice parameter of bulk Cu is larger than that of Ni. The average grain sizes of

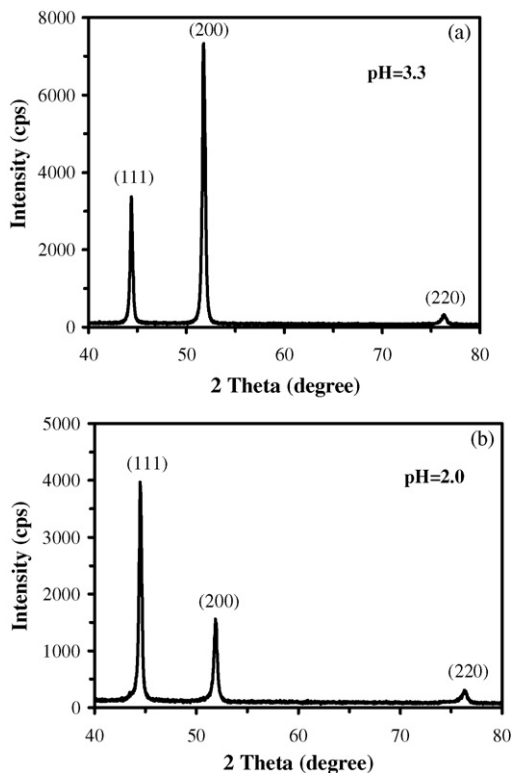


Fig. 1. XRD patterns of Ni–Cu films electrodeposited (a) at high pH 3.3 and (b) at low pH 2.0.

the crystallites were determined using the line broadening of the observed peaks according to the Sherrer formula [8]. The full width at half-maxima (FWHM) of the peaks was estimated after the correction for the instrumental line broadening. The grain sizes were found to be about 120 nm for the sample grown at high pH and 90 nm for that at low pH, that is, at high pH level the grains are larger than those at low pH. This may be a result of the growth processes occurred depending on the electrolyte pH.

The texture formation of films was evaluated by considering, the integral peak intensities of $\{111\}$, $\{200\}$ and $\{220\}$ reflections and comparing them with those of Ni (or Cu) having completely random oriented grains. Since the integral intensities of the $\{220\}$ planes in all films remains weaker compared to those of the $\{111\}$ and $\{200\}$ ones, it is reasonable to consider and compare only the integral intensity ratios of the $\{200\}$ and $\{111\}$ planes. The data obtained from XRD patterns are given in Table 1. As seen from the table, for the film grown at high pH, the ratio of the integral intensity of the 200 peak to that of the 111 one, I_{200}/I_{111} , is 2.36, which is larger than the 0.46 value of completely random oriented Ni (or Cu), while for the film at low pH, it is almost the same as in a powder pattern of bulk Ni (or Cu) [8]. This indicates that the texture formation of Ni–Cu films changes depending on the electrolyte pH. At high pH, the $\{110\}$ texture of the fcc structure is predominant, while at low pH the crystal planes are oriented randomly as a powder pattern. It has been reported that the electrolyte pH hardly affects the crystallographic structure of Ni–Cu alloy films, which were deposited on Cu substrates using some complexing agents [9]. The different

Table 1
Structural and magnetic data obtained from electrodeposited Ni–Cu films

Samples	pH (± 0.1)	$I_{(200)}/I_{(111)}$	XRD		EDX (%atom)		AMR (%)		Coercivity (kOe)	
			Lattice parameter $a \pm \Delta a$ (nm)	Grain size (nm)	Ni	Cu	LMR (+)	TMR (–)	Parallel	Perpendicular
Ni–Cu films	3.3	2.36	0.3523 ± 0.0009	120	81.7	18.3	2.5	2.5	0.08	0.18
	2.0	0.46	0.3519 ± 0.0006	90	93.2	6.8	3.3	3.3	0.08	0.18
Bulk Cu (or Ni)	[8]	0.47	0.3615 (0.3524)	–	–	–	–	–	–	–

behaviour of our films, from those observed in Ref. [9], may be due to the bath type and/or the substrate used, because Ni–Cu films usually grow adopting the crystal structure of Cu substrates [5,10]. However, the textured structure of films electrodeposited on several polycrystalline substrates is known to evolve depending on deposition conditions such as the electrolyte composition, pH, deposition potential and additives. The change in the texture degrees of films deposited from the electrolytes based on Ni has been usually attributed to the presence of inhibiting species such as hydrogen and nickel hydroxide [11,12]. Such species can be formed depending on the electrolyte composition and deposition parameters, and can be adsorbed partially on the cathode surface. The amount of inhibiting species can be change with the electrolyte pH.

The effect of the electrolyte pH on the surface morphology of the Ni–Cu films was studied using SEM. Fig. 2(a) and (b) show the SEM images of films deposited at high pH and low pH levels, respectively. The surface morphology is clearly seen to be strongly influenced by the electrolyte pH. At high pH (3.3), the films have a morphology consisting of round and dendritic shapes. The size of the crystallites in white regions vary between 600 and 3200 nm, while that of those in the dark regions is between 100 and 150 nm. At low pH (2.0), the film surface is generally smoother and more uniform, but the shapes like a cauliflower in some regions appears. These white coloured crystallites have sizes ranging from 500 to 2000 nm, while the crystallites in the dark regions are between 100 and 500 nm in size. These values are generally much larger than the actual grain sizes obtained from the XRD patterns (see Table 1). We believe that small crystallites are dominant for the XRD measurements, whereas the SEM images reflect the crystallites appeared only on the surface of the film.

The change of the surface morphology with the electrolyte pH may be explained by the hydrogen evolution occurred at the cathode surface. If the hydrogen evolution, which is favoured at low pH, is sufficiently effective, then it changes the electrochemical conditions at the vicinity of the cathode. This may lead to the formation of different dendrites. Very recent studies showed that electrochemical conditions such as surface pH and overpotential affect the structure of electrodeposited metal films [13,14].

As well as possessing different microstructural properties, Ni–Cu films grown at low and high pH levels also have different magnetic and magnetotransport properties. The room temperature magnetoresistance curves of the films grown at high pH and low pH are shown in Fig. 3(a) and (b), respectively. The percentage changes in the VDP resistance, MR (%), as a function of the

applied magnetic field, were calculated according to the relation $MR(\%) = \{[R(H) - R_{\min}]/R_{\min}\} \times 100$, where $R(H)$ is the value of the resistance at any magnetic field and R_{\min} is the value at the field where the resistance is minimum. Ni–Cu alloy films produced at both high and low pH levels exhibited anisotropic magnetoresistance (AMR). The behaviour observed in the AMR is similar those observed in ferromagnetic materials such as Ni, Co, Ni–Co and Ni–Cu [1,2,15]. As seen from the figures, as the magnetic field increases, the longitudinal magnetoresistance (LMR) (dashed line) increases, while the transverse magnetore-

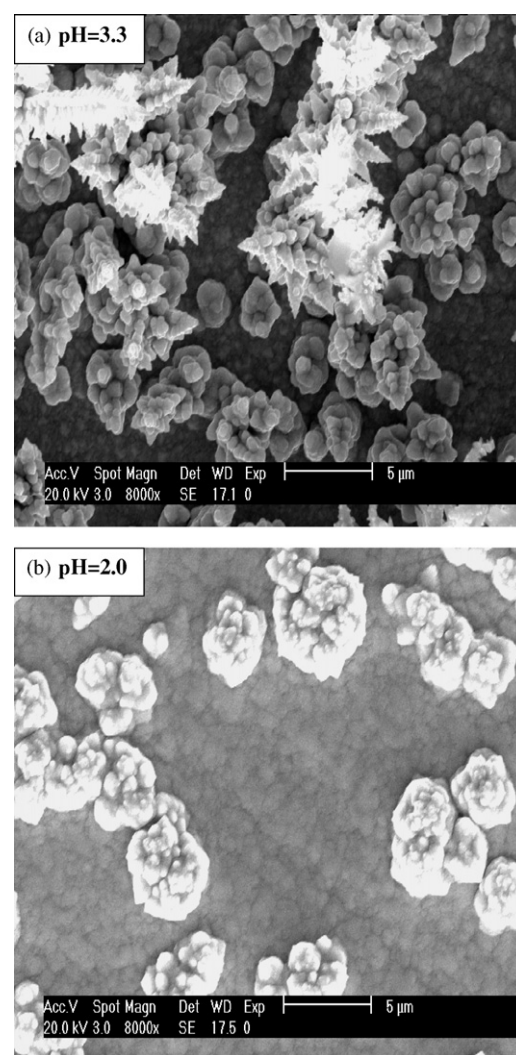


Fig. 2. SEM micrographs for the Ni–Cu films electrodeposited (a) at high pH 3.3 and (b) at low pH 2.0.

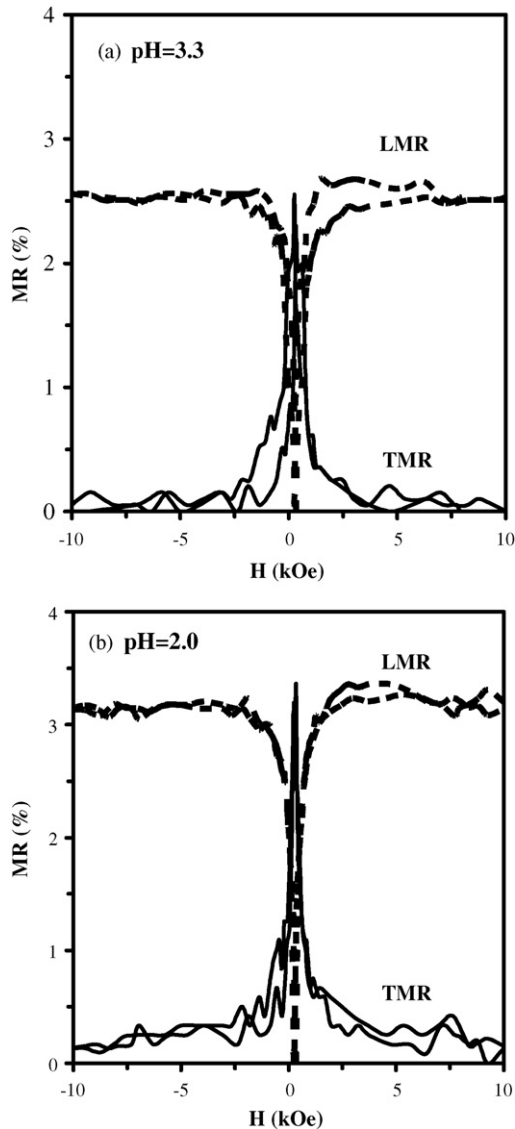


Fig. 3. Magnetoresistance curves of Ni–Cu films electrodeposited (a) at high pH 3.3 and (b) at low pH 2.0. The solid line indicates the transverse magnetoresistance (TMR) and the dashed line is the longitudinal magnetoresistance (LMR).

sistance (TMR) (solid line) decreases. The AMR magnitudes are also given in Table 1. Since the percentage changes in VDP resistances are not necessarily equal to the percentage changes in true longitudinal and transverse resistances [7,16], therefore it must be careful when comparing MR ratios obtained using the VDP method to those obtained by other methods. For the sample at each pH, positive longitudinal and negative transversal MR ratios are almost of the same order, which is in agreement with those expected from theoretical studies of AMR [17,18]. The LMR and TMR values ($\sim 3.3\%$) of the samples grown at low pH are larger compared to those ($\sim 2.5\%$) of the samples at high pH, i.e. decreasing electrolyte pH enhances the AMR effect of Ni–Cu films. This may be attributed to the differences in the texture degrees of the films as well as the Cu content, because it is well known that different orientations give different contributions to the AMR [17] and it also changes with the Cu concentration [15].

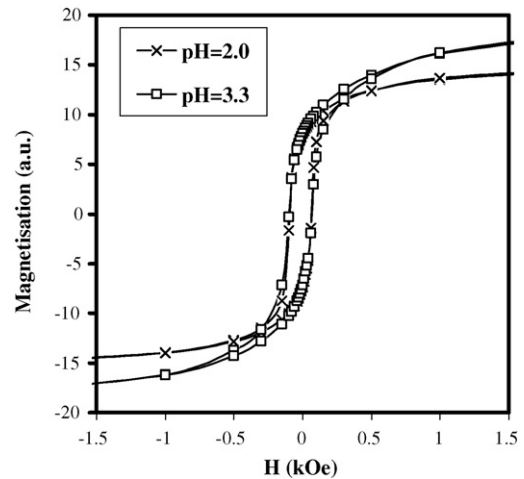


Fig. 4. In-plane hysteresis loops of Ni–Cu films electrodeposited at high pH 3.3 and low pH 2.0.

Magnetisation measurements were performed to examine in-plane and out-of-plane anisotropies as well as the coercivities. In-plane hysteresis loops of Ni–Cu films deposited at pH 3.3 and 2.0 are shown in Fig. 4. The coercivities of the films are quite close to each other and around 0.08 kOe, regardless of electrolyte pH. However, saturation magnetisation is different for the films grown at high and low pH. At the pH 3.3, the loop has an anisotropy field of 0.88 kOe, whereas at low pH (2.0), the loop exhibits a smaller anisotropy field, 0.45 kOe, both of which are larger than their own coercivities. These results show that the samples at high pH are harder to magnetise compared to those at low pH. A possible explanation may be that the degrees of texturing for the deposits at low and high pH are different. As mentioned earlier, the $\{111\}$ texture at low pH is stronger, which is the easy axis for bulk Ni [19]. When the field is applied perpendicular to the film plane, the coercivities reach a value of around 0.18 kOe, indicating the film has a planar magnetic anisotropy.

4. Conclusions

Single Ni–Cu films were electrodeposited on polycrystalline Ti substrates from electrolytes with two different pH values. To the XRD data, the $\{100\}$ texture of the fcc structure in the films grown at high pH (3.3) develops preferentially, while for the films at low pH (2.0) the crystal planes are randomly oriented as in a powder pattern of bulk Ni (or Cu). The SEM images showed that the surface morphologies of Ni–Cu films are significantly affected by the electrolyte pH. When the films are grown at high pH, they have rougher surfaces and consist of larger crystallites compared to those grown at low pH. Magnetoresistance measurements made at room temperature indicated that Ni–Cu films have an anisotropic magnetoresistance effect. The AMR and magnetic properties of the films also change with the electrolyte pH. The differences observed in the magnetic and magnetotransport behaviours were attributed to the microstructural changes caused by from the electrolyte pH and/or the Cu content.

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References

- [1] T.R. McGuire, R.I. Potter, *IEEE Trans. Magn.* 11 (1975) 1018.
- [2] E. Tóth-Kadar, L. Péter, T. Becsei, J. Tóth, L. Pogány, T. Tarnóczy, P. Kamasa, I. Bakonyi, G. Láng, A. Cziráki, W. Schwarzacher, *J. Electrochem. Soc.* 147 (2000) 3311.
- [3] S. Kainuma, K. Takayanagi, K. Hisatake, T. Watanabe, *J. Magn. Magn. Mater.* 246 (2002) 207.
- [4] F. Ebrahimi, Z. Ahmed, *J. Appl. Electrochem.* 33 (2003) 733.
- [5] M. Alper, W. Schwarzacher, S.J. Lane, *J. Electrochem. Soc.* 144 (1997) 2346.
- [6] M. Alper, K. Attenborough, V. Baryshev, R. Hart, D.S. Lashmore, W. Schwarzacher, *J. Appl. Phys.* 75 (1994) 6543.
- [7] W. Schwarzacher, D.S. Lashmore, *IEEE Trans. Magn.* 32 (1996) 3133.
- [8] B.D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley Publishing, Reading, MA, 1978.
- [9] I. Mizushima, M. Chikazawa, T. Watanabe, *J. Electrochem. Soc.* 143 (1996) 1978.
- [10] G. Nabyouni, W. Schwarzacher, *J. Magn. Magn. Mater.* 156 (1996) 355.
- [11] C. Bergenstorf Nielsen, A. Horsewell, M.J.L. Østergård, *J. Appl. Electrochem.* 27 (1997) 839.
- [12] K.C. Chan, W.K. Chan, N.S. Qu, *J. Mater. Process. Technol.* 89–90 (1999) 447.
- [13] M. Motoyama, Y. Fukunaka, T. Sakka, Y.H. Ogata, *J. Electrochem. Soc.* 153 (2006) C502.
- [14] N.D. Nikolic, K.I. Popov, Lj. J. Pavlovic, M.G. Pavlovic, *Surf. Coat. Technol.* 201 (2006) 560.
- [15] R.M. Bozorth, *Ferromagnetism*, Van Nostrand, New York, 1951, p. 745.
- [16] C. Prados, D. Garcia, F. Lesmes, J.J. Freijo, A. Hernando, *Appl. Phys. Lett.* 67 (1995) 718.
- [17] S. Chikazumi, *Physics of Magnetism*, Wiley, New York, 1964, p. 419.
- [18] Th. G.S.M. Rijks, R. Coehoorn, M.J.M. de Jong, W.J.M. de Jonge, *Phys. Rev. B* 51 (1995) 283.
- [19] J. Crangle, *The magnetic Properties of Solids*, Edward Arnold, London, 1977, p. 6.