



Preparation, corrosion and structural properties of Cu–Ni multilayers from sulphate/citrate bath

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ABSTRACT

Potentiostatic electrodeposition was used to produce Cu–Ni multilayer by two-wave pulse plating technique from sulphate/citrate electrolyte at pH 4. Cyclic voltammetry studies provide information about the deposition potential. The compositions of multilayers were studied using X-ray fluorescence (XRF). Electrochemical corrosion studies of the deposited multilayer on copper were studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The surface of the layer having smooth, small grain and compact structure was confirmed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis. The face centered cubic lattices are present in the Ni–Cu multilayer and this is confirmed by the X-ray diffraction (XRD) data. The multilayer structures have better corrosion resistance than the base substrate.

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1. Introduction

There has recently been a growing interest in electrodeposited multilayer [1], especially since it has been demonstrated [2,3] that they can exhibit a significant giant magnetoresistance (GMR) effect. Therefore, Cu–Ni multilayer obtained by pulse electrodeposition methods has been studied. The properties of the multilayer deposits are significantly affected by parameters such as the electrolyte concentration, pH, and the deposition potential, additive, substrates and the control methods (potentiostatic and galvanostatic). The effect of these parameters has been studied extensively [4,5–13]. A complexing agent is required for the deposition of Cu–Ni multilayer; cyanide [14], citrate [15,16], pyrophosphate [17], and glycine [18] were studied as the complexing agent. The sulphate/citrate electrolyte can produce Cu–Ni multilayer of high structural quality [19].

In this perspective, the present work aims to study the formation of Cu–Ni multilayers from the sulphate/citrate electrolyte by two-wave pulse plating technique and evaluates their characteristic properties. The tri-sodium citrate was chosen as the complexing agent due to its ability to improve the deposition efficiency, to obtain stress free deposits and its relatively less toxic nature [15].

2. Experimental

Cu–Ni multilayers were deposited on Cu foil substrate. The Cu foil substrate was mechanically polished and degreased with

acetone in order to remove the impurities. The substrate surface was then electrochemically cleaned with alkali solution and chemically treated for few seconds in 10% H₂SO₄. Pulse electrodeposition of the Cu–Ni multilayer was carried out using the electrolyte that contains CuSO₄, NiSO₄ and tri-sodium citrate. Deionized water was used to prepare the electrolyte solution. The deposition was carried out in a three-electrode cell system under potentiostatic control using Parstat 2273 model electrochemical analyzer. A platinum sheet was used as a counter electrode (anode). The cathode (Cu foil substrate) potentials are referred to a saturated calomel electrode (SCE). Deposition of Cu layer was carried out at the cathode potential –0.4 V (vs SCE), while the deposition of Ni layer was –1.19 V (vs SCE) and pH 4. The corrosion behavior of the multilayer was studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) using Parstat 2273 Princeton advanced electrochemical system. The structure of the multilayer was studied using X-ray diffractometer. The surface morphology of the deposited multilayers was examined with SEM and AFM.

3. Result and discussion

The Cu–Ni multilayer deposits from the sulphate/citrate bath was adherent smooth and bright in appearance. The compositions of the deposits were measured by using X-ray fluorescence, these results shows that the percentage of Cu in the deposit is 62% and Ni is 38%. The multilayer deposits samples were bent through 180° angle and deposit shows no lifting and peeling, which shows good adhesion of these coatings on the copper substrates. Deposits with a Vickers hardness of 291 HV (25 g) were obtained.

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This higher value of hardness for the multilayer is due to the smaller crystal size of the deposits and they are in the order of nanometers.

3.1. Electrochemical characterization

In order to obtain preliminary information about the deposition processes and to choose the appropriate deposition potentials, the solution was first characterized by cyclic Voltammetry (CV). The stabilized CV curve was obtained for the solution at pH = 4 and are shown in Fig. 1. The potential sweep rate was 10 mV/s, the potentials scan was started in the cathodic direction (from 0.8 to -1.6 V vs SCE) the peak appeared in the cathodic side at -0.4 V vs SCE corresponding to the reduction of Cu^{2+} ion. Another peak was appeared at -1.19 V vs SCE for the reduction of Ni^{2+} ion. In reverse direction the anodic peak seen at about 0.3 V vs SCE is due to the Cu dissolution. Since no Ni dissolution peak is observed, it can be concluded that the Ni remain passive. These results are good agreement with Bready et al. [20], in that Ni dissolution starts at a potential, which is by 1.2 V vs SCE, more positive than Cu^{2+}/Cu equilibrium potential in the same solution. Based on CV measurements the appropriate potential range to deposit Cu and Ni were fixed.

Fig. 2 shows the potentiodynamic polarization curves of the uncoated and coated Cu–Ni multilayer on copper substrate in 3.5 wt.% NaCl solution at room temperature. The corrosion resistance of the Cu–Ni/Cu is significantly improved which can be observed by a shift of the whole polarization curve towards the region of higher potential. The values of corrosion potentials are -242 mV vs SCE and -177 mV vs SCE for the uncoated and multilayer coated samples, respectively. The corrosion potential of the coated sample shifted in the noble direction by 65 mV vs SCE than

the uncoated sample. The porosity of the coatings is determined using the formula

$$P = (R_{p,S}/R_p)10^{-|\Delta E_{\text{corr}}|/b_a}$$

where $R_{p,S}$, substrate polarization resistance; R_p , coatings polarization resistance; ΔE_{corr} , potential difference between the coatings and substrate and b_a , anodic slope for substrate.

The porosity of Cu–Ni multilayer is 0.13%. The much of lower porosity indicate the Cu–Ni multilayers are showing better corrosion resistance.

The electrochemical impedance spectrum of Cu–Ni multilayers system was measured with the same three-electrode assembly as used for the potentiodynamic polarization experiment. The impedance measurement was performed in 3.5 wt.% NaCl solution at the corrosion potential. Fig. 3 shows the comparative Nyquist impedance response of the Cu–Ni multilayer and uncoated samples. The value of the charge transfer resistance (R_{ct}) is 190.4Ω and double layer capacitance (C_{dl}) is 1.306 mF for the uncoated samples, 693.2Ω , and $111.7 \mu\text{F}$ for the Cu–Ni multilayer sample, respectively. The R_{ct} value of Cu–Ni multilayer is high compared to that of uncoated Cu substrate and C_{dl} value of Cu–Ni multilayer is lower than Cu substrate. From these values, it can be concluded that the Cu–Ni multilayer has high corrosion resistance.

3.2. X-ray analysis

The X-ray diffractogram (XRD) for the Cu–Ni multilayer is shown in the Fig. 4. There are eight peaks in this spectrum, four peaks correspond to Cu and another four peaks to Ni and these peaks are arranged alternatively, Cu and Ni indexed as face cen-

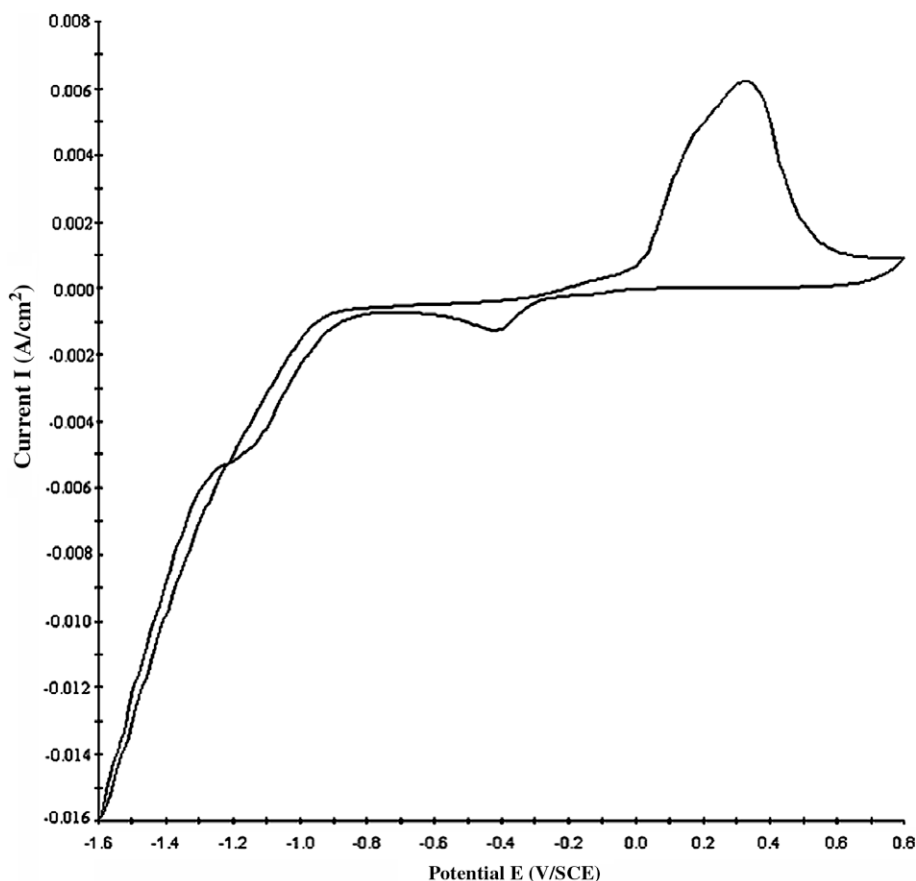


Fig. 1. Cyclic voltammetric curve of sulphate/citrate bath obtained at scan rate of 10 mV/s.

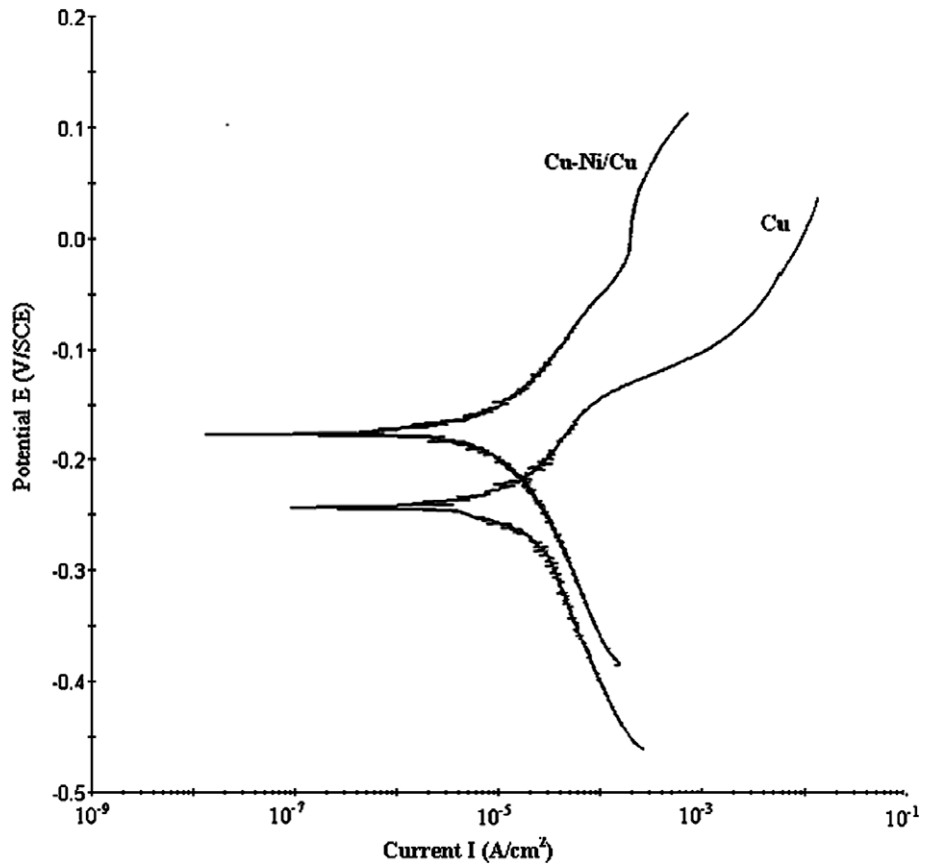


Fig. 2. Potentiodynamic polarization curves of the Cu–Ni/Cu and Cu.

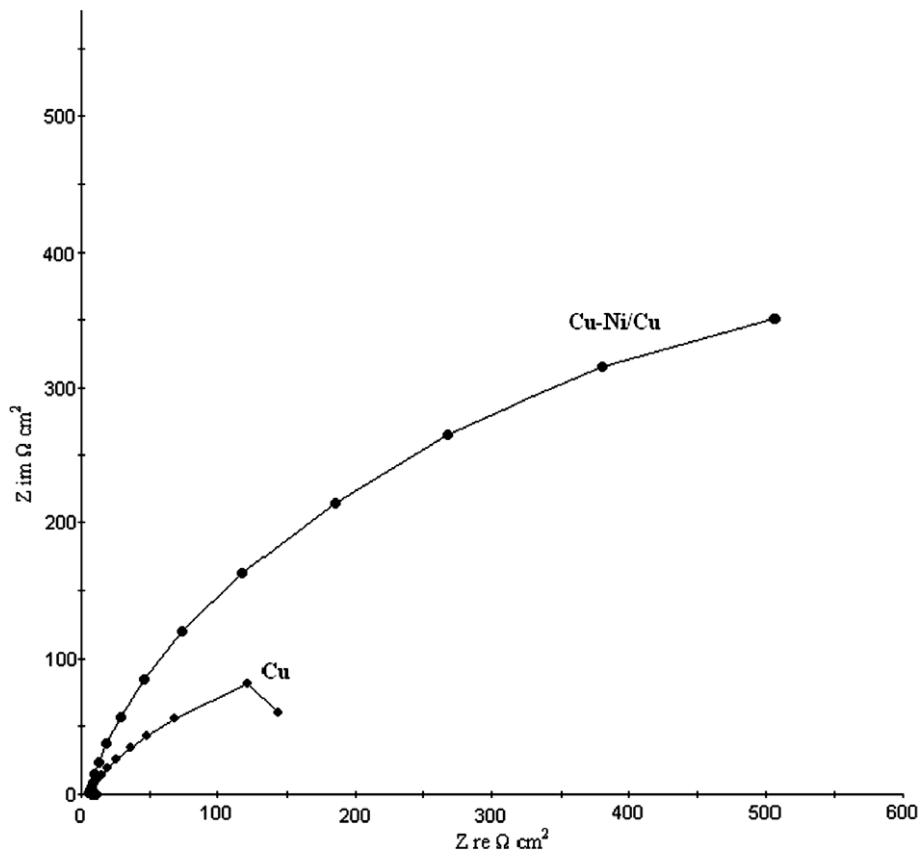


Fig. 3. Electrochemical impedance spectra of the Cu–Ni/Cu and Cu.

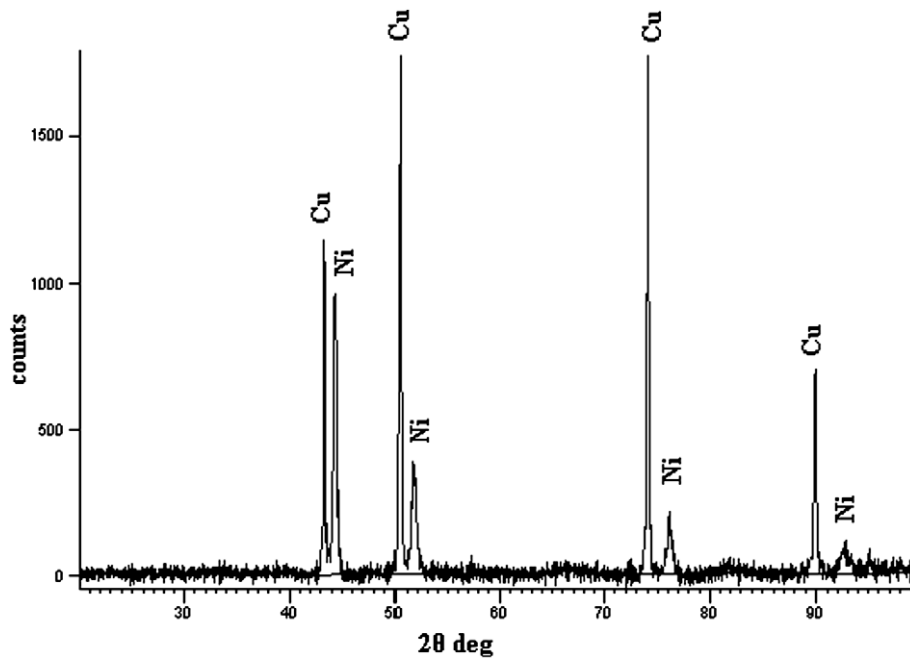


Fig. 4. X-ray diffractogram of Cu–Ni multilayer deposit.

Table 1

Data analysis from XRD pattern in Fig. 4.

Peak	2 theta(°) from Fig. 5	2 theta(°) from JCPDS	d spacing from Fig. 5 (Å)	d spacing from JCPDS (Å)	Indices
1	43.2838	43.33	2.08864	2.088	Cu ₍₁₁₁₎
2	44.3149	44.54	2.04240	2.034	Ni ₍₁₁₁₎
3	50.3924	50.48	1.80941	1.808	Cu ₍₂₀₀₎
4	51.7071	51.89	1.76645	1.762	Ni ₍₂₀₀₎
5	74.0812	74.20	1.27876	1.278	Cu ₍₂₂₀₎
6	76.0656	76.44	1.25026	1.246	Ni ₍₂₂₀₎
7	89.8819	90.03	1.09049	1.090	Cu ₍₃₁₁₎
8	92.6332	93.04	1.06517	1.062	Ni ₍₃₁₁₎

tered cubic lattice. These results confirm that there is no alloy formation, i.e., each separate metal is only present. The XRD results are correlated with standard JCPDS data as given in Table 1. The data shows that the observed inter planar distance (d) values are in good agreement with the standard (d) values of the corresponding phases. The most intense peak is (2 2 0) for Cu and (1 1 1) for Ni. Crystalline size was calculated by using Scherrer's formula from the full width at half maximum (β) of the peaks expressed in terms of radian

$$D = 0.94\lambda/\beta \cos \theta$$

The average calculated crystalline size of the Cu and Ni layer are 50 and 30 nm. Such small crystalline sizes contribute to the smooth surface morphology and also they have a beneficial effect on the improvement of micro hardness of the coatings [21]. Also the crystalline size in the nano meters range results in considerable improvement in their corrosion resistance [22]. The strain and dislocation density are determined using the formula [23],

$$\varepsilon = \beta \cos \theta/4 \text{ and } \delta = n/D^2$$

where β is the FWHM of (2 2 0) peak, D is crystalline size and n is a factor, which is unity for thin film [24]. The calculated value of the strain for copper and nickel are 6.6×10^{-2} and 3.2×10^{-2} and the dislocation density values are 2.7×10^{-4} and 1.1×10^{-4} . These smaller values indicate high quality deposits.

3.3. Surface morphology

The surface morphology of the Cu–Ni multilayer deposit formed by two-wave pulse plating techniques is studied by SEM analysis. On analyzing the microstructures shown in Fig. 5, it is found that

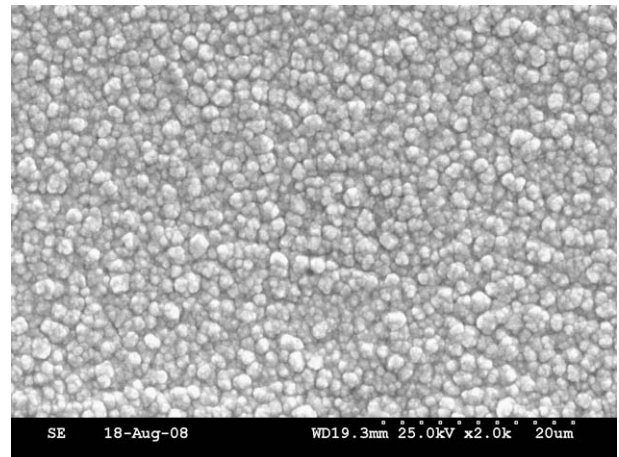


Fig. 5. Scanning electron microscopy images of the Cu–Ni multilayer.

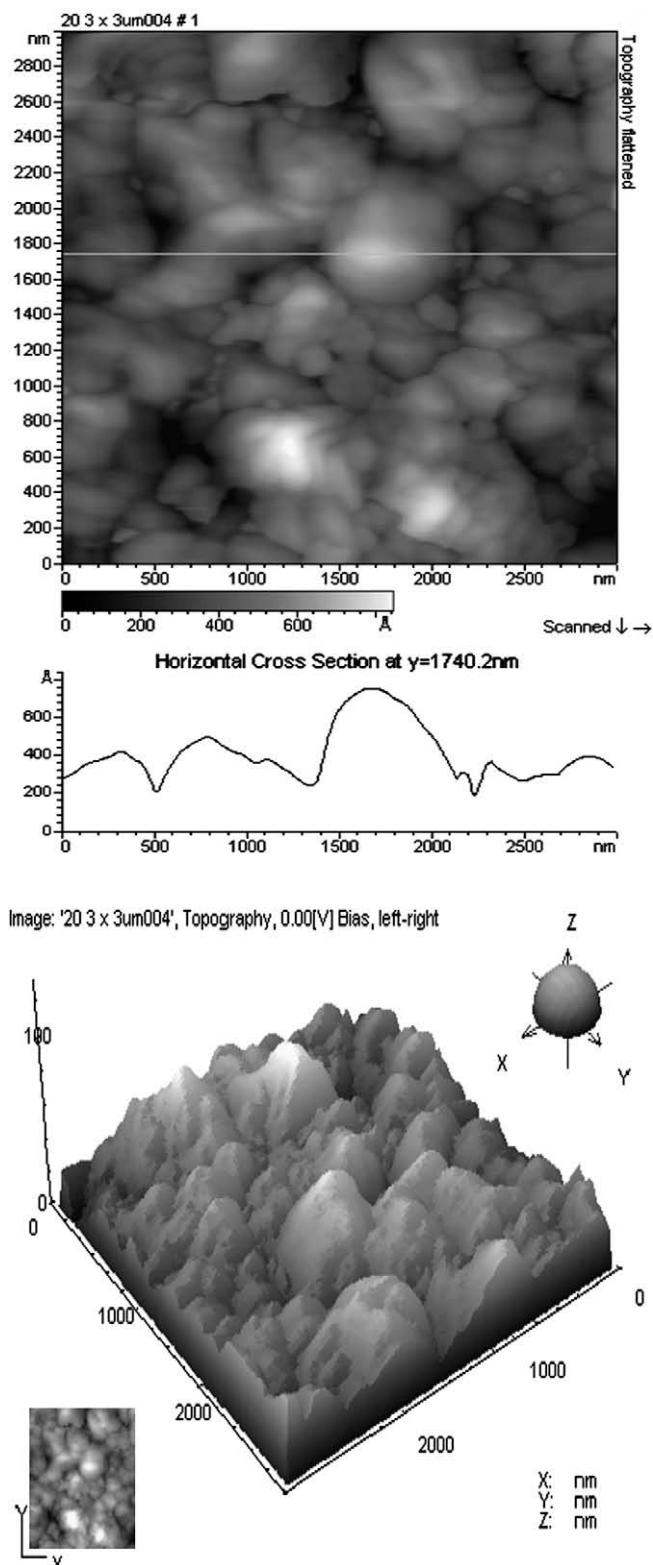


Fig. 6. Atomic force microscopy images of Cu–Ni multilayer.

the Cu–Ni multilayer deposits were compact and consisted of fine grains covering the whole substrates. The average grain size is 1–3 μm from SEM images for the Cu–Ni multilayer. The smaller grain size is facilitating the better electrochemical performance. The surface topography of the multilayer was carried out using atomic force microscopy (AFM). The advantage of AFM is its capacity to probe minute details related to the individual grains region

and inter grains. A representative AFM picture scanned over an area of $5 \times 5 \mu\text{m}$ of the sample prepared is shown in Fig. 6. These images show that the deposit is having finer nodular grains in the range of 100–500 nm and uniform coverage.

From this AFM analysis, the average roughness (R_a) value of coatings was calculated as the deviation in height from the profile mean value [25]

$$R_a = 1/N \sum_0^N |Z_i - Z|$$

where Z_i , the height of the each pixel position along the line profile; Z , the mean height and N , number of pixel along the each line scan of the profile.

The roughness value of the alloy deposition is 0.15 μm . This much of small value indicate the deposition are smoother.

4. Conclusion

Adherent, smooth and bright deposits of Cu–Ni multilayer coatings were two-wave pulse plated successfully on copper substrates from sodium citrate based baths. Uniform coverage with spherical nodular morphology and smoothness of these coatings is observed from microstructure analysis. The Cu–Ni multilayer deposits, obtained from bath composition and bath parameters are mentioned and demonstrated excellent corrosion protective performance.

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References

- [1] C.A. Ross, *Ann. Rev. Mater. Sci.* 24 (1994) 159.
- [2] M. Alper, K. Attenborough, R. Hart, S.J. Lane, D.S. Lashmore, C. Younes, W. Schwarzacher, *Appl. Phys. Lett.* 63 (1993) 2144.
- [3] W. Schwarzacher, D.S. Lashmore, *IEEE Trans. Magn.* 32 (1996) 3133.
- [4] S.K.J. Lenczowski, C. Schonenberger, M.A.M. Gijs, W.J.M. de Jonge, *J. Magn. Mater.* 148 (1995) 455.
- [5] L. Peter, Z. Kupay, A. Cziraki, J. Pader, J. Toth, I. Bakonyi, *J. Phys. Chem. B* 105 (2001) 10867.
- [6] I. Bakonyi, J. Toth, L. Goulou, T. Becsei, E. Toth-Kadar, W. Schwarzacher, G. Nabyouni, *J. Electrochem. Soc.* 149 (2002) C195.
- [7] W.R.A. Meuleman, S. Roy, L. Peter, I. Varga, *J. Electrochem. Soc.* 149 (2002) C479.
- [8] M. Shima, L. Salamanca-Riba, R.D. McMichael, T.P. Moffat, *J. Electrochem. Soc.* 149 (2002) C439.
- [9] G. Nabyouni, O.I. Kasyutich, S. Roy, W. Schwarzacher, *J. Electrochem. Soc.* 149 (2002) C218.
- [10] M. Alper, W. Schwarzacher, S.J. Lane, *J. Electrochem. Soc.* 144 (1997) 2346.
- [11] G. Nabyouni, W. Schwarzacher, *J. Magn. Mater.* 156 (1996) 355.
- [12] E. Chassaing, A. Morrone, J.E. Schmidt, *J. Electrochem. Soc.* 146 (1999) 1794.
- [13] V. Weihnacht, L. Peter, J. Toth, J. Padar, Zs. Kerner, C.M. Schneider, I. Bakonyi, *J. Electrochem. Soc.* 150 (2003) C507.
- [14] L.E. Stout, O.G. Burch, A.S. Langdorf, *Trans. Electrochem. Soc.* 57 (1930) 113.
- [15] I. Baskaran, T.S.N. Shankara Narayanan, A. Stephen, *Mater. Lett.* 60 (2006) 1990.
- [16] W.R.A. Meuleman, S. Roy, L. Peter, I. Bakonyi, *J. Electrochem. Soc.* 151 (2004) C256.
- [17] M. Ishikawa, H. Enomoto, *J. Met. Finish. Soc. Jpn.* 31 (1980) 545.
- [18] I. Mizushima, Masatoshi Chikazawa, Tohru Watanabe, *J. Electrochem. Soc.* 143 (1996) 1978.
- [19] A. Cziraki, V. Pierron-Bohnes, C. Ullag-Bouillet, E. Toth-Kadar, J. Bakonyi, *Thin Solid Films* 318 (1998) 239.
- [20] P. Bready, S. Roy, D. Landalt, *J. Chem. Soc. Faraday Trans.* 92 (1996) 4015.
- [21] S.H. Kim, U. Erb, K.T. Aust, F. Ganzalaz, G. Palumbo, *Plat. Surf. Finish.* 5 (2004) 68.
- [22] Haichuan Mu, Jin Seok, R.Y. Lin, *J. Electrochem. Soc.* 150 (2) (2003) C67.
- [23] G.B. Williamson, R.C. Smallman, *Philos. Mag.* 1 (1956) 34.
- [24] V. Senthilkumar, S. Venkatachalam, C. Viswanathan, S. Gopal, Sa.K. Narayanadass, D. Mangalaraj, K.C. Wilson, K.P. Vijayakumar, *Cryst. Res. Tech.* 40 (2005) 573.
- [25] James R. Smith, Steven Breakspear, Seelagh A. Cambell, *Trans. Inst. Met. Finish.* 81 (2003) B55.