Evolution of nanostructures, mechanical and magnetic properties in electrochemically deposited Cu/Ni multilayers under ultrasound

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ABSTRACT

In this work an attempt has been made to synthesize Cu/Ni multilayer by electrochemical route under ultrasound varying for alternate deposition of nano-layers. Our conclusions are the result of combining experimental work and characterization with XRD, SEM, AFM. XRD and microscopic studies confirmed the nano-range deposits. Ultrasound was found to have significant effect on the quantity of materials deposited and the surface morphology. Force-displacement curves generated during loading and unloading of a diamond tip indenter were used to determine the hardness and elastic properties of the deposits. An enhancement in the hardness was observed with increasing layer quantity. We have also demonstrated the increase in GMR values in multilayers.

INTRODUCTION

Historically electrolytic deposition was the earliest technique utilized to fabricate the multiyaers. The recent development of more advanced methods in electrolytic deposition made it worthwhile to reinvestigate this technique. One such advances, sonoelectrochemistry (electrochemistry under ultrasound) has been acknowledged long back. In general, the imposition of ultrasound on electroplating systems gives rise to an increase of effective current density and changes in chemical and physical properties of deposited films (Walker and Walker, 1972). While ultrasound strongly affects mass transfer processes the effects of ultrasound on charge transfer processes in sluggish electrochemical systems are still uncertain (Hyde and Compton, 2002). The tribological properties of these layered structures directly depend on the layer properties, e.g., the layer thickness, surface roughness, coefficient of friction, hardness, stiffness and elastic modulus ratios of the layers to the substrate (Cammarata et al., 1990). Extrinsic magnetic properties play a major role in determining the performance of multilayers (kadar et al., 2000) as magnetic recording media and magnetic sensors. Like other magnetoresistive effects; giant magnetoresistance (GMR) is the change in electrical resistance of some materials in response to an applied magnetic field. It was discovered that the application of a magnetic field to magnetic

metallic multilayers in which ferromagnetic layers are separated by nonmagnetic spacer layers of a few nm thick, results in a significant reduction of the electrical resistance of the multilayer. Based upon the above discussion of the versatile properties and applications of multilayer metallic systems, we have made an approach to synthesize Cu/Ni multilayers with an extreme control of thickness and purity of each of the layers in the presence of ultrasound. The mechanical and magnetic properties are explored.

EXPERIMENTAL DETAILS

Experiments were performed on graphite andcopper substrates of exposed surface area of 1 cm × 1 cm. A platinum rod of 0.2 cm diameter and an Ag/AgCl electrode (Eco Chemie, Netherlands) served as counter and reference electrodes respectively. Ultrasound irradiation was accomplished by an ultrasonic cleaner of 30 kHz frequency (EI2LH). Electrochemical measurements were conducted using a potentiostat/galvanostat (Eco Chemie Netherland, Autolab PGSTAT 12). X-ray diffraction (XRD) patterns were recorded from 40˚ to 80˚ with a Philips X-pert MPD system diffractometer using Cu K_α at an accelerating voltage of 40 kV at a counting rate of 2 °/min. Microscopic studies were done by a JEOL 6480 LV scanning electron microscope (SEM). A SIEKO SPA 400 atomic force microscope (AFM) with a silicon probe was used to take the AFM figures. Mechanical properties were studied by nanoindentation. The tests are done with a constant maximum load of 10 mN applied to the substrate and the displacement is recorded for each of the temperatures. The GMR measurement was done using the four point contact method by using the instrument EECS 143 model.

RESULTS AND DISCUSSIONS

3.1. Selection of Electrolyte

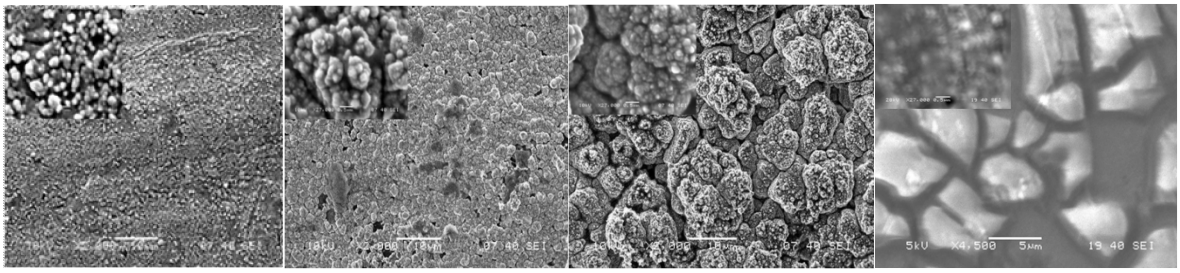

Figure 1. SEM topography of multilayers (a) Cloride, (b) Sulphate, (c) Watt's and (d) Sulfamate baths.

A critical topographical surface analysis has been done for choosing the most appropriate electrolyte for the multilayer deposition. The topographical images are shown in Fig. 1. All the surface images are in presence of ultrasound. It can be observed from the figure that the surface finish from chloride bath appears to be smooth at macroscopic level. But the magnified images indicate that the deposit from watts solution is more compact and seems to be free from any residual stress unlike the typical nickel electrodeposit from the sulfamate bath. So for further experimentation watts bath is chosen.

3.2. Electrochemical Analysis

Fig. 2 shows the CV for both the metals at a temperature of 55˚C in silent as well as sonication conditions. The sweep was done for the redox potential range of − 1.5 V to + 2 V for complete analysis of both the metals. For deposition of nickel it can be seen that the current flown at the final negative vertex potential is 350 mA in US field as compared to 200 mA of silent deposit. The cycle in US condition appears to be charge transfer controlled because of absence of cross over point in the voltammogram. Sharp nickel dissolution peak can be observed in the CV plot. There is no sharp appearance of copper deposition or dissolution peak in the test because of the low concentration of the ions. However a CV has been conducted to confirm the copper redox reaction as demonstrated in the inset of the figure. The potential is varied in between − 0.7 V to 1.5 V. The voltammogram confirms copper reduction from − 0.17 V to − 0.6 V and showing two minima around +0.017 V and − 0.35 V. It is reasonable to assume that the two minima are due to the reduction of Cu^{+} and Cu^{2+} ions. The current observed form the peak potential is around 4 mA. The copper oxidation peaks are also prominent.

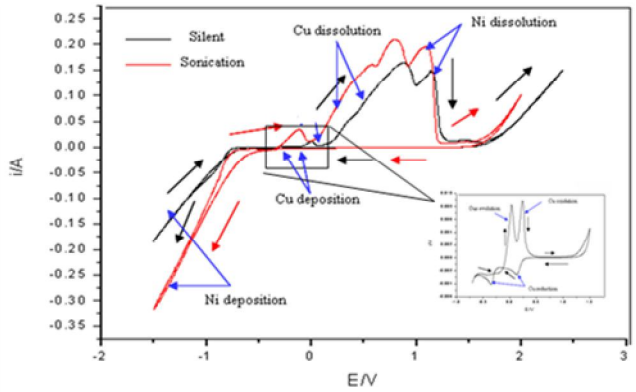

Figure 2. Cyclic Voltammetry of Cu and Ni form Watt's bath.

Hence as the dissolution peaks of both the metals are nearly same, the peaks have overlapped showing a single peak for both the metals. Based upon the above observations we have chosen the currents for the chronopotentiometry methods to control the thickness of each of the layers. Current pulses and time duration chosen are 225 mA and 4 mA & 0.2 s and 20 s for Ni and Cu respectively.

3.3. Phase and surface analysis

Fig. 3 shows the XRD phase analysis of the deposit at room temperature in both conditions. The diffraction peaks corresponding to 2θ = 43.298, 50.434, 74.132 are copper peaks having the JCPDS card no. 04-0836. Similarly for nickel the peaks are of 2θ = 44.497, 51.850, 76.383 having the JCPDS card no. 87-0712. From the plot it can be observed that the peaks are sharp for both the metals indicating the high crystallinity of the metallic phases. However the intensity of nickel phase in silent conditions is not prominent. The fact behind the observation may be that the deposition is not appropriate in silent condition at room temperature.

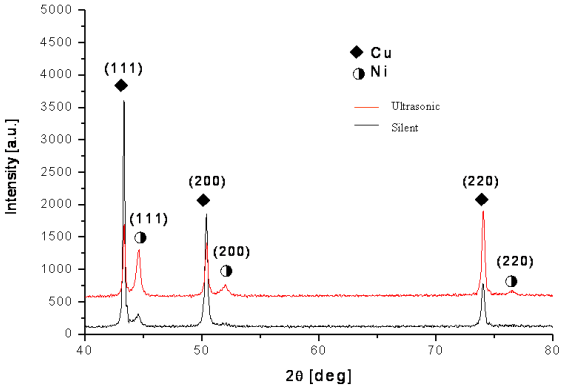

Figure 3. XRD pattern of the multilayers.

Fig. 4 illustrates the deposition of watt's bath in the absence and presence of ultrasound at room temperature. The deposition for watt's bath is showing non-uniform spherical grains in silent condition. Room temperature watt's bath in sonication condition produces higher surface finish and crystalline form with the requirement of finer grains, in nano-range, with compact structure comparison to silent deposit. The low temperature insonation deposit is a morphology with a basic characteristic of the grains almost spherical, finer, high surface smooth, minimized void space with the consecutive grains sintered to give the compact crystalline surface as reported by the authors for copper deposits (Mallik and Ray, 2009). Comparison to the low temperature silent and ultrasonic conditions the, sonication condition showing higher compact and uniform structure. The AFM analysis of the surface morphology further compliments the findings from SEM as shown in the figure.

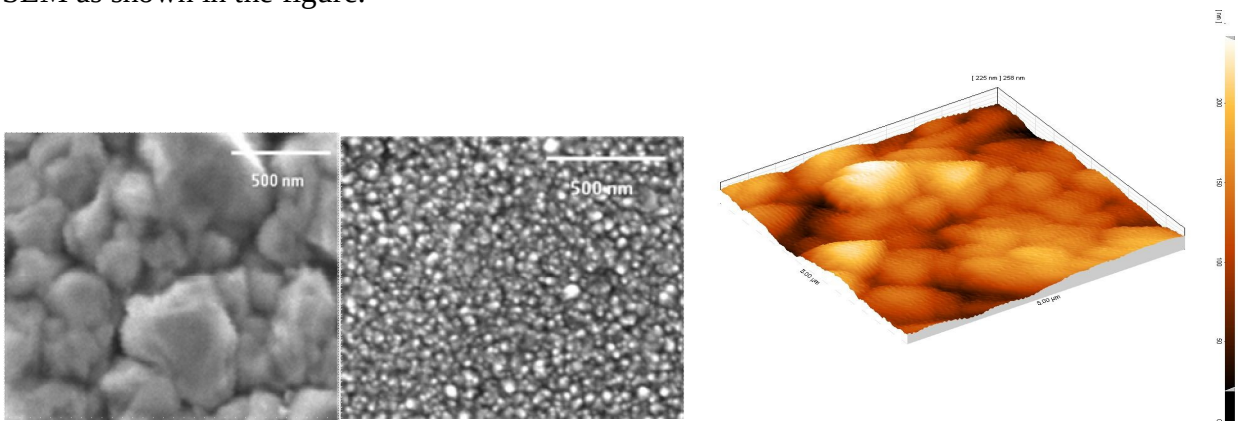

Figure 4. SEM and AFM topography of multilayers

3.4. Texture analysis

Fig. 5 represents the texture analysis of the deposits with their respective ODF data with nickel top and copper top surfaces deposit to correlate the hardness data with the preferred oriented

planes. The pole figures with their corresponding scattered orientation levels are represented clearly in figure. (022) plane is having the highest scattered orientation whereas (111) plane is having the least one. So we conclude that the nickel ions have arranged themselves to grow in the most favorable plane, the highest packing plane i.e. (111).

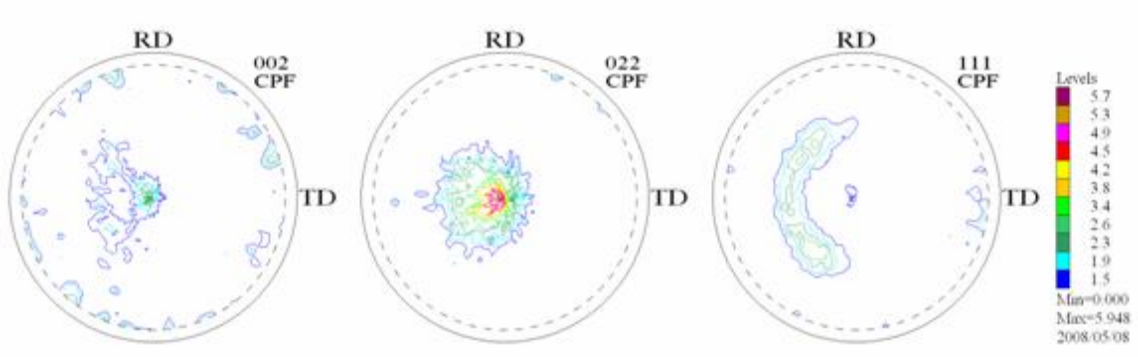

Figure 5. Pole figure of Ni surface

3.5. Hardness Analysis

Hardness values are outputted directly by the software. The software also produces loading and unloading curves, and the hardness depth curves as presented in Fig. 6. The average hardness values of the samples are presented in Table 1. It can be observed that the bilayer has a hardness value, 1.884 GPa, higher than the individual values of the metallic deposits. And the multilayer has even higher value than the bilayers. To study the substrate effects we have compared the hardness values onto a copper substrate. It shows the prominent substrate effect on the strength of the multilayers deposited.

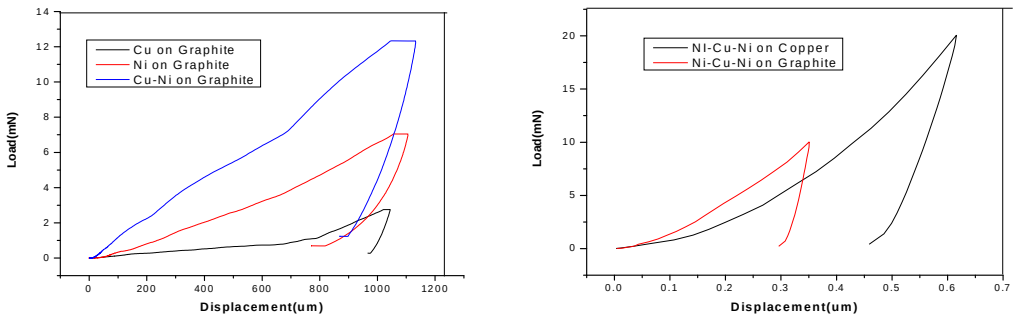

Figure 6. Load-Unloading curve for multilayers

The hardness value of the bilayer is of higher order and almost average of the hardness of the single layers of copper and nickel. The slope of the uploading graphs giving the value of the elastic modulus value of the bilayer is the average of the elastic modulus of the single layers. The

load–unloading graph for multilayer on graphite substrate and copper substrate are also shown in the figure. The graphs showing the same result as predicted from the theoretical prediction. The multilayer formation on copper substrate is giving higher order hardness (3.5585 GPa) comparison to that on graphite substrate (2.8204 GPa). This can be attributed both to grain size strengthening (small grains compared to the grain size of pure crystalline copper or nickel) and/or strain hardening. The grain size strengthening is determined by the strength of Cu grains (H_0) and the average grain size (d) of Cu according to the Hall-Petch relation ($H = H_o + kd^{-1/2}$), where k, Hall-Petch coefficient accounting the grain boundary resistance to dislocation movement. The strain-hardening effect can easily be described by the Taylor relation.

Table 1. Measured hardness values for Cu/Ni multilayers

Item	Copper	Nickel	Cu/Ni bilayer	Multilayer	
				Graphite	Copper
H in GPa	0.205	0.513	1.884	2.8204	3.5585

3.6 Resistivity and GMR Analysis

The multilayer sample prepared in presence of ultrasound was investigated for the GMR measurement. In absence of magnetic field the variation of the current with potential is ohmic as shown in the graph of Fig. 10 . The variation of the resistance with the presence of magnetic field in the longitudinal direction of multilayers is also shown in the figure.

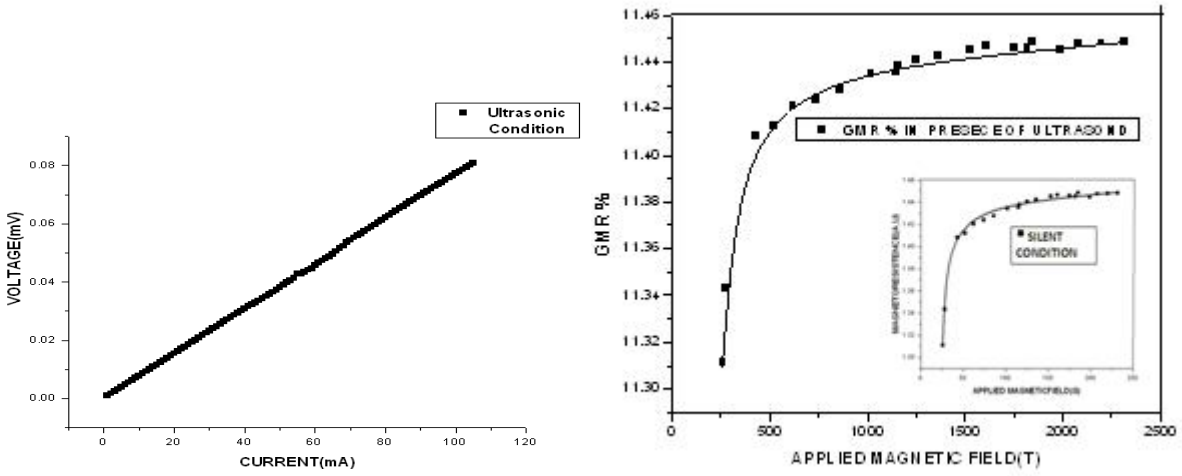

Figure 7. Linear Ohmic variation and GMR value vs. longitudinal magnetic field

The magnetic resistance value of the multilayer sample deposited at silent condition and low magnetic field showing magneto resistance variation, but not giving the giant value. This results matches with the previous result of the interfacial irregularities at silent condition of the deposit

giving rise to the low variation of the magnetoresistance. Since the interface plays an important role in the variation of the magnetoresistance during the spin pinning state from one layer to the other the interfacial irregularity hamper the pinning percentage so as to the magnetoresistance. The variation of the magnetoresitance variation of giant value at the ultrasonic condition confirms a 10 fold increase in the magneto resistance. As established from the previous data the presence of ultrasound gives the cleaner and coherent interface. So due to the presence of cleaner and coherent interface the spin pinning from one layer to the other will be easier depending on the spin orientation of the consecutive nickel layers.

CONCLUSION

Multilayered of Cu/Ni with a sublayer thickness in the nano order have been successfully sonoelectrochemically deposited from various baths like sulphate, chloride, suffamate and watt's bath. Because of the better surface finish watts bath has been chosen for experimentation. The deposit was done onto graphite as well as copper substrates. With a careful CV study the deposition current was chosen. The study showed that the appropriate current for nickel was 225 mA and for copper it was 4 mA. Deposition time was maintained for 0.2 s and 20 s for Cu and Ni for equal thickness respectively. The multilayer thicknesses were crucially controlled by a well formulated mechanism by the potentiostatic and galvanostatic application. However we experimented with 10 layers of each of the phase. The phase analysis was done exclusively by X-ray diffraction (XRD). XRD result confirms the presence of both the phases. Microstructure is characterized by SEM and AFM. Texture study was done by small angle X ray study. Hardness was done by a nanoindentor. And the magnetic properties were studied by the conventional four probe analysis method. The watts bath at different temperature showed difference in microstructure in sonicated and silent condition. As explained by various authors the deposit obtained at low temperature was black and appears to be powdery as compared to sonicated low temperature, giving better microstructure. The morphology is in nanorange is confirmed by the microscopic analysis. Hardness values are found to be enhanced with increased number of layers i.e. from a value of 0.205 GPa to 3.558 GPa. The effect of different substrate like copper and graphite are investigated. The formation of multilayer over the copper substrate gives superlattice structure with enhanced hardness. The GMR measurement at silent and ultrasonic condition gives several fold (10) increase in GMR value in sonicated condition.

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