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Pulsed Electrodeposition of Cu, Ni-Cu

Introduction:

Electrodeposition is a process for producing dense, uniform, smooth, adhering coating of metals or alloy on a substrate with the use of electric field. According to the nature of applied electric field, the deposition may be, potentiostatic (deposition at constant DC potential), galvanostatic (deposition at constant DC current) and pulsed. Deposition of metals/alloy carried out using pulsed current or potential is the pulse electrodeposition (PED). A pulsed electrodeposition has various advantages over conventional DC. For example, the deposits obtained via PED are compact with low porosity, less stress, less voids, smooth, homogenous and thermally stable. [1-2] Recently, pulse electrodeposition technique is being used to get micro or nanostructured coating or thin films of binary, ternary or higher order alloys on the metallic substrate.[3-6] Microstructure and texture may also vary by varying substrate, plating bath chemistry, temperature, additives and pH.[7] PED in recent years has gained extensive attention as it is cost effective and easy to perform and many times the deposits obtained exhibits excellent mechanical and electrical strength. For example, Nano twinned copper deposited by Lu et.al using PED exhibits ultrahigh strength and electrical conductivity.[8]

The present report is on pulse electrodeposition of Copper and Ni-Cu on the stainless steel substrate with current density of $100 mA/cm^2$, pulse on time of 10 ms and off time of 90 ms. The faculty intern also attempted to evaluate the role of pH on the deposition of Ni-Cu binary alloy from the citrate bath.

Sample Preparation and Experiment Setup.

Cu and Ni-Cu were deposited on carbon steel substrate under different pH condition. For this, steel substrate of dimensions 5 x 3.2 cm^2 was taken and polished using SiC emery paper from grit size of 1000, 1500, 2000 to get scratch-free mirror like surface. The polished substrates were further processed by sonication for 1 h in acetone to remove any dirt or grease. Finally, specimens were immersed into DI water and sonicated for another 1 h. The substrates were insulated by polyimide tape exposing a 1x1 cm^2 area for deposition, also another end of the substrate was left exposed for passing current. For carrying out the deposition, Dynatronix DuPR10-3-6XR pulse power supply was used. The negative terminal of power supply was connected to substrate (cathode) and positive terminal was connected to anode. All the electrodeposition experiments were carried out at room temperature.

Electrodeposition of copper (N1)

To carry out electrodeposition of copper, electrolyte i.e. 0.1 M CuSO$_4$.5H$_2$O (2g CuSO$_4$.5H$_2$O /80ml DI water) was prepared and the pH was adjusted to 1 by addition of conc. sulfuric acid. Oxygen free high conductivity copper wire was used as anode, while stainless steel was used as cathode. Deposition of copper was carried out in a glass beaker containing electrolyte (80 ml) under galvanostatic mode with current density of 100 mA/cm^2 and deposition time of 15 min. Pulse on and off time were 10 ms and 90 ms respectively.

Electrodeposition of Ni-Cu at pH 1 (N2)

Electrolytic solution (80 ml) was prepared from 0.1 M CuSO$_4$.5H$_2$O (2g CuSO$_4$.5H$_2$O /80ml DI water), 0.5 M NiSO$_4$.7H$_2$O (11.2g NiSO$_4$.7H$_2$O /80 ml DI water) and 11.2 g sodium citrate. The pH of the solution was adjusted to 1 by addition of sulfuric acid. Nickel (99%) was used as anode, while stainless steel was used as cathode. Deposition was carried out in a glass beaker containing electrolyte under galvanostatic mode with current density of 100 mA/cm^2 and deposition time of 30 min. Pulse on and off time were 10 ms and 90 ms respectively.

Electrodeposition of Ni-Cu at pH 8 (N3)

Electrolytic solution (80 ml) was prepared from 0.1 M $CuSO_4.5H_2O$ (2g $CuSO_4.5H_2O$ /80ml DI water), 0.5 M $NiSO_4.7H_2O$ (11.2g $NiSO_4.7H_2O$ /80 ml DI water) and 11.2 g sodium citrate. The pH of the solution was adjusted to 8 by addition of 25 % NH_3 solution. Nickel (99%) was used as anode, while stainless steel was used as cathode. Deposition was carried out in a glass beaker containing electrolyte under galvanostatic mode with current density of 100 mA/cm^2 and deposition time of 30 min. Pulse on and off time were 10 ms and 90 ms respectively.

Once the deposition time is over the substrate was removed from the electrolytic bath and dipped into DI water and dried. The elemental analysis and the composition of deposited sample were determined by energy dispersive X- Ray spectroscopy (EDXS). Morphology of the deposited sample were analyzed by field emission scanning electron microscopy (FESEM). Root mean square roughness was obtained through AFM study.

Result and discussion

Composition/ Microstructure / Surface roughness analysis:

Coating of copper metal and Ni-Cu alloy on the steel substrate was verified by EDX analysis. The EDX analysis of sample N1 shows the presence of Copper (98% at. wt.) as demonstrated in Fig.1. From the EDX it is very clear that the coating contains primarily copper as expected from the copper sulphate electrolytic bath. Moreover, a small percentage of iron (2% at. wt.) is due to the steel substrate, on which the electrodeposition has been carried out. EDX analysis of Ni-Cu deposition obtained at different pH was also carried out to find out the percentage composition of each metal in the deposit. Ni-Cu alloy coating obtained from electrolytic bath (0.1 M $CuSO_4.5H_2O$, 0.5 M $NiSO_4.7H_2O$, 0.5 M sodium citrate) at pH 1 and pH 8 were labelled as N2 & N3, respectively. EDX analysis of N2 and N3 shows that in both the cases there was successful inclusion of Ni and Cu on the steel. The Nickel content were 6 and 43% (at. wt.) for the deposits obtained at pH 1 & 8, respectively (Fig. 2 & 3 respectively). It should be noted that in spite of higher concentration of Nickel ion in the electrolytic bath, it is the copper that is preferentially deposited on the steel. The preferential deposition of copper compared to nickel is due to the higher standard electrode potential of copper, +0.34 V compared to Nickel, -0.25 V. So, to carry out the

codeposition of Nickel and Copper, it is necessary to add complexing agent, sodium citrate in presence of ammonia, because it shift the standard electrode potential of copper toward more negative side facilitating the codeposition of Cu & Ni.[9] As the pH increases, the stability of copper complex also increases and that is why at higher pH the standard electrode potential of copper shifts toward more negative side, increasing the content of Nickel in deposit at higher pH.[10] Surface morphology of electrodeposited copper, for sample N1 obtained after 15 min. of deposition time, was characterized through FESEM as depicted in fig.4a. There was uniform coating of copper that covers the entire steel substrate. A plate like morphology was observed and the surface appeared rough. To study the morphology of Ni-Cu deposits obtained through deposition time of 30 min, the FESEM micrographs of N2 and N3 were also analyzed and it also shows uniform deposition like N1 (Fig 4b & 4c) but surface appeared smoother and cauliflower shape. The surface roughness for deposits was found out by AFM instrument. For N1 and N2, it was not possible to measure the surface roughness as the coating adhered to the substrate strongly and did not peel off from the substrate. Moreover, the substrate being bulky in size cannot be used directly for AFM investigation. For N3 we were able to peel off the film from the substrate and the film was used for measurement of surface roughness. The surface topography of N3 as measured by AFM, at scan rate of 0.7 Hz is shown in Fig. 5. The images reveal a uniform and continuous microstructures with grain size in nm range. The statistical root mean square (RMS) roughness (R_q) was found 22 nm.

Conclusion

Cu as well as Ni-Cu, were successfully deposited on steel substrate ($1{\times}1$ cm^2) by pulsed electrodeposition. For co-deposition of Ni and Cu, a complexing agent, sodium citrate was used. It was observed that the use of sodium citrate at low pH (1) resulted in deposition of mainly copper and very less Nickel i.e. 6% (at.). As we increased the pH to 8, Nickel content in the deposit increased to 43 % (at.). The SEM revealed plate like morphology for copper deposit, while cauliflower like morphology for Ni-Cu deposit. For Ni-Cu deposit at pH 8, the statistical root mean square roughness was 22 nm.

References

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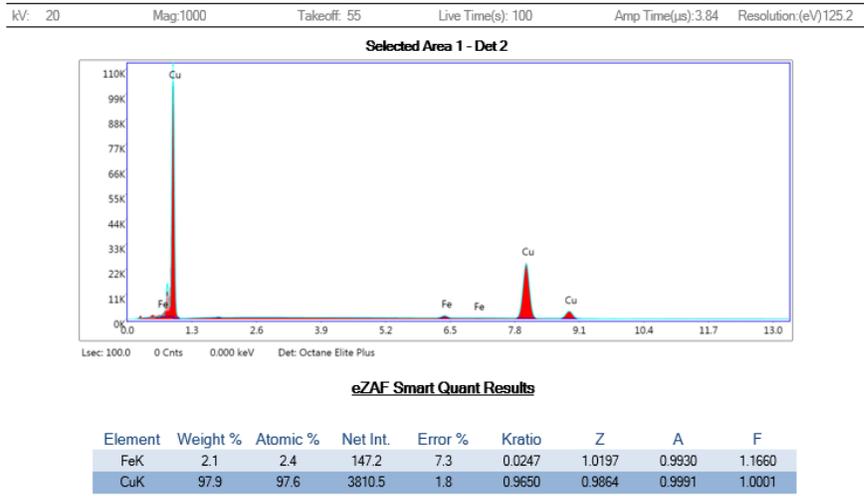10. H. Natter and R. Hempelmann, *J. Phys. Chem.* **100**, 19525 (1996).
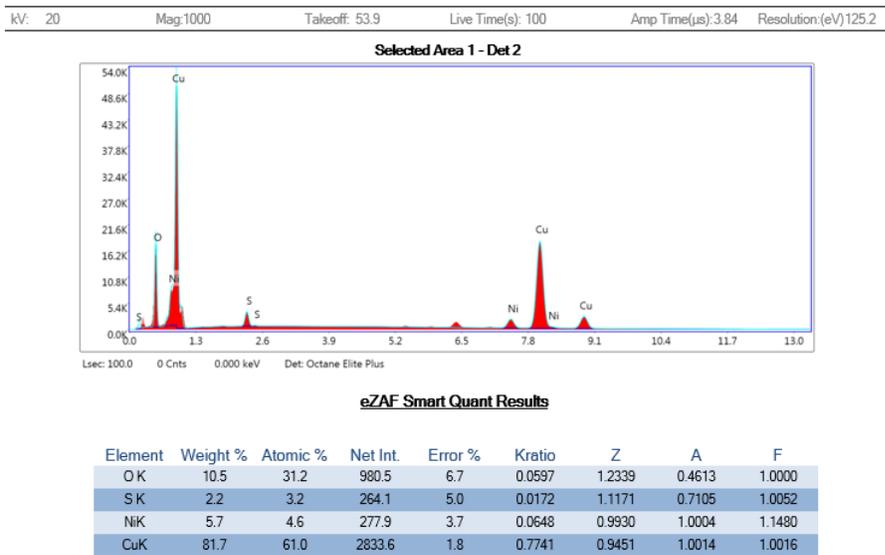
Figures

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
FeK	2.1	2.4	147.2	7.3	0.0247	1.0197	0.9930	1.1660
CuK	97.9	97.6	3810.5	1.8	0.9650	0.9864	0.9991	1.0001

Fig. 1. EDX analysis of sample N1

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	10.5	31.2	980.5	6.7	0.0597	1.2339	0.4613	1.0000
S K	2.2	3.2	264.1	5.0	0.0172	1.1171	0.7105	1.0052
NiK	5.7	4.6	277.9	3.7	0.0648	0.9930	1.0004	1.1480
CuK	81.7	61.0	2833.6	1.8	0.7741	0.9451	1.0014	1.0016

Fig.2. EDX analysis of sample N2

Selected Area 1 - Det 2

Lsec: 100.0   0 Cnts   0.000 keV   Det: Octane Elite Plus

eZAF Smart Quant Results

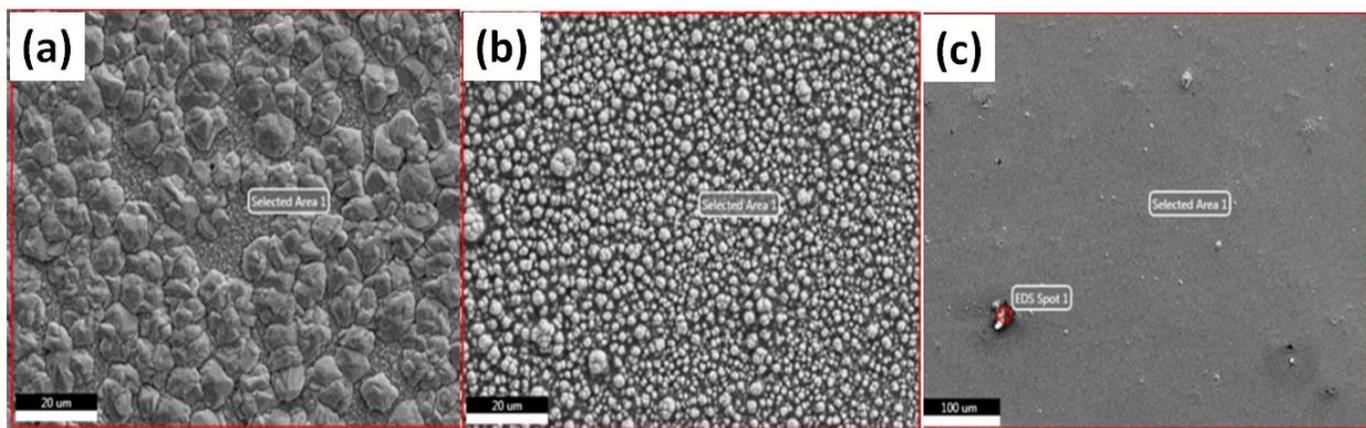| Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
NiK	43.1	45.1	2089.6	2.0	0.4543	1.0144	0.9997	1.0386
CuK	56.9	54.9	2155.5	1.9	0.5485	0.9660	0.9974	1.0011

Fig.3. EDX analysis of sample N3

Fig.4. SEM micrograph of pulsed electrodeposited Cu , Ni-Cu on stainless steel substrate at 100 mA/cm^2 , T_{ON}=10ms,T_{OFF}=90ms (a) Cu (pH 1, deposition time 15 min) (b) Ni-Cu (pH 1, deposition time 30 min) (c) Ni-Cu (pH 8, deposition time 30 min)
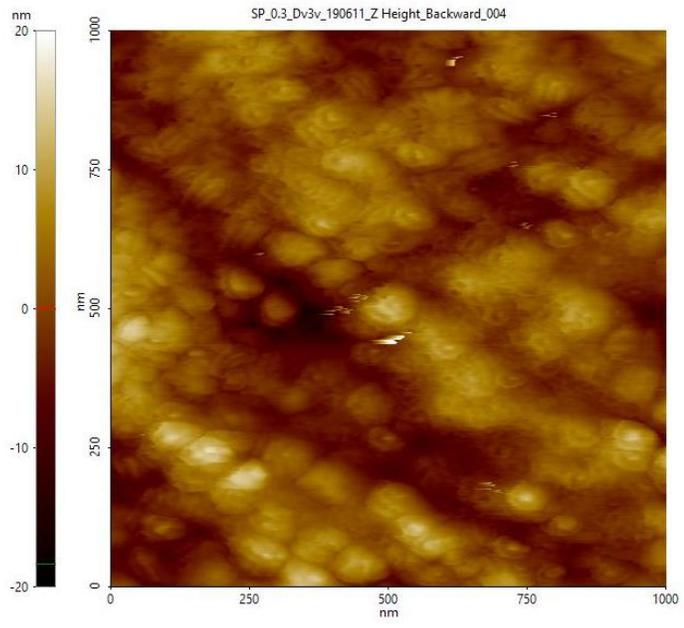
Fig.5. AFM image of Ni-Cu deposit at pH 8 (N3)